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August 2, 2011

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Kansas City District
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ATTN: CENWK-PM-ES/Buckrucker
CONTRACT: W912DQ-08-D-0018
PROJECT: Lower Passaic River Restoration Project
Remedial Investigation/Feasibility Study Oversight
Lower Passaic River Study Area, New Jersey
SUBJECT: Final Quality Assurance Project Plan, Addendum #8
Chemical Water Column Monitoring Study/Small Volume Chemical
Data Collection

Dear Ms. Buckrucker:

CDM Federal Programs Corporation (CDM) is pleased to submit this electronic copy of the Final Quality Assurance Project Plan, Addendum No. 8 for the Oversight of Remedial Investigation/ Feasibility Chemical Water Column Monitoring Study/ Small Volume Chemical Data Collection in support of the Lower Passaic River Restoration Project in the Lower Passaic River Study Area, New Jersey. This document is based on the CPG's *Quality Assurance Project Plan/Field Sampling Plan Addendum Remedial Investigation Water Column Monitoring/ Small Volume Chemical Data Collection* dated July 2011.

If you have any comments concerning this submittal, please contact me at (212) 377-4056.

Very truly yours,
CDM FEDERAL PROGRAMS CORPORATION

A handwritten signature in black ink, appearing to read "C. Tsang", is written over a horizontal line.

Frank Tsang, P.E.
Task Order Manager

Attachment

cc: A. Yeh, EPA
S. Vaughn, EPA
Bill Sy, EPA
J. Czapor, CDM (Letter Only)

S. Budney, CHMM, CDM
J. Oxford, CHMM, CDM
G. Molnar, CDM
Project File

Contract No.: W912DQ-08-D-0018
Task Order No.: 014

U. S. Army Corps of Engineers
Kansas City District

**Final Quality Assurance Project Plan
Addendum No.8
Chemical Water Column Monitoring
Study/ Small Volume Data Collection**

Lower Passaic River Restoration Project
Remedial Investigation/Feasibility Study
Oversight

Lower Passaic River Study Area, New
Jersey

August 2, 2011

CDM

**LOWER PASSAIC RIVER RESTORATION PROJECT
OPERABLE UNIT (OU) 2**

**Remedial Investigation/Feasibility Study Oversight
Final Quality Assurance Project Plan
Addendum No.8**

Chemical Water Column Monitoring Study/ Small Volume Data Collection

Lower Passaic River Study Area, New Jersey

USACE CONTRACT No. W912DQ-08-D-0018

TASK ORDER No. 014

August 2, 2011

**Prepared for:
U.S. Army Corps of Engineers
Kansas City District**

**Prepared by:
CDM
110 Fieldcrest Avenue, 6th Floor
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Note:

Worksheets not included herein are included in the Physical Water Column Monitoring/Generic Final QAPP dated March 9, 2010.

Acronyms

%	percent
%D	percent difference
%R	percent recovery
µg/L	microgram per liter
A	analytical
ABS	absolute difference
ANSETS	Analytical Services Tracking System
ASC	analytical services coordinator
ASTM	American Society of Testing and Materials
Axys	Axys Analytical Services Limited
CA	corrective action
CAS	Chemical Abstract Service
CCV	continuing calibration verification
CD	compact disk
CDM	CDM Federal Programs Corporation
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	chain of custody
CPG	Cooperating Parties Group
CRM	certified reference material
CRQL	contract required quantitation limits
CVAFS	cold vapor atomic fluorescence spectrometry
CWCM	Chemical Water Column Monitoring
DESA	Division of Environmental Science and Assessment
DL	detection limit
DOC	dissolved organic carbon
DQA	data quality assessment
DQI	data quality indicators
DQL	data quality level
DQO	data quality objectives
DV	data validation
EPA	United States Environmental Protection Agency
EQulS	Environmental Quality Information System
FASTAC	Field and Analytical Services Teaming Advisory Committee
FID	flame ionization detector
FS	feasibility study
FTL	field task leader
GC/MS	gas chromatograph / mass spectroscopy

HCL	hydrochloric acid
HDPE	high density polyethylene
Hg	mercury
HRGC/HRMS	High Resolution Gas Chromatography / High Resolution Mass Spectrometry
HRGC/LRMS	High Resolution Gas Chromatography / Low Resolution Mass Spectrometry
HNO ₃	nitric acid
ICP	inductively coupled plasma
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICV	initial calibration verification
IMDL	Inter-Laboratory method detection limit
IPR	initial precision and recovery
KC	Kansas City
LCS	laboratory control samples
LIMS	laboratory information management system
LPR	Lower Passaic River
LPRSA	Lower Passaic River Study Area
MB	method blank
MDL	method detection limit
mg/L	milligram per liter
MPC	measurement performance criteria
MS	matrix spike
MS/ MSD	matrix spikes /matrix spike duplicate
NA	not available or not applicable
ng/L	nanogram per liter
NJ	New Jersey
NJDEP	New Jersey Department of Environmental Protection
NJDOT	New Jersey Department of Transportation
NOAA	National Oceanic Atmospheric Administration
NY	New York
°C	degrees Celsius
OPR	ongoing precision and recovery
OU	operable unit
PAH	polycyclic aromatic hydrocarbon
PAL	project action limit
PCB	polychlorinated biphenyl
PCDD/PCDF	polychlorodibenzodioxin /polychlorodibenzofurans
PE	performance evaluation

pg/g	picogram per gram
PM	project manager
POC	particulate organic carbon
PQLG	project quantitation limit goal
PREmis	Passaic River Estuary Management Information System
PWCM	Physical Water Column Monitoring
QA	quality assurance
QAC	quality assurance coordinator
QAPP	quality assurance project plan
QC	quality control
QCS	quality control sample
QL	quantitation limit
R	recovery
RI/FS	Remedial Investigation / Feasibility Study
RPD	relative percent difference
RPM	remedial project manager
RRF	relative response factor
RSCC	Regional Sample Control Coordinator
RSD	relative standard deviation
S&A	sampling and analytical
SIM	selective ion monitoring
SM	Standard Method
SOP	standard operating procedure
SOW	scope of work
SSC	suspended solids concentration
SVOC	semivolatile organic compound
TAL	target analyte list
TBD	to be determined
TDS	total dissolved solids
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
TSOP	Technical Standard Operating Procedure
TSS	total suspend solids
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
WS	worksheet

Dioxin and Furans:

HpCDD	hepta-chlorodibenzo- <i>p</i> -dioxin
HpCDF	hepta-chlorodibenzofuran
HxCDD	hexa-chlorodibenzo- <i>p</i> -dioxin
HxCDF	hexa-chlorodibenzofuran
OCDD	octa-chlorodibenzo- <i>p</i> -dioxin
OCDF	octa-chlorodibenzofuran
PeCDD	penta-chlorodibenzo- <i>p</i> -dioxin
PeCDF	penta-chlorodibenzo-furan
TCDD	tetrachloro-dibenzo- <i>p</i> -dioxin
TCDF	tetrachloro-dibenzo-furan

Introduction

CDM Federal Programs Corporation (CDM) will accept split chemical water column study aqueous samples from the Cooperating Parties Group (CPG) upon completion of the study in the Lower Passaic River Study Area (LPRSA).

This Final Quality Assurance Project Plan (QAPP) Addendum No.8 and the *Lower Passaic River Remedial Investigation / Feasibility Study (RI/FS) Oversight Final QAPP, Physical Water Column Monitoring and Generic Information for Upcoming Tasks*, dated March 2010 (hereafter referred to as the Final QAPP) are the governing documents for execution of this analytical investigation. CDM will use the various plans prepared by the CPG contractors to verify proper execution of the chemical water column study sample handling, preservation and shipment.

The CDM Final QAPP indicated that future oversight tasks assigned to CDM would be appended with selected worksheets. The following worksheets are included in this addendum to reflect only the chemical water column study analytical procedures and requirements of the CPG's QAPPs written by AECOM, *Quality Assurance Project Plan/Field Sampling Plan Addendum Remedial Investigation Water Column Monitoring/ Small Volume Chemical Data Collection* dated July 2011:

- | | |
|-----------------|-----------------|
| ▪ Worksheet #1 | ▪ Worksheet #18 |
| ▪ Worksheet #2 | ▪ Worksheet #19 |
| ▪ Worksheet #3 | ▪ Worksheet #20 |
| ▪ Worksheet #9 | ▪ Worksheet #23 |
| ▪ Worksheet #10 | ▪ Worksheet #24 |
| ▪ Worksheet #11 | ▪ Worksheet #28 |
| ▪ Worksheet #12 | ▪ Worksheet #29 |
| ▪ Worksheet #14 | ▪ Worksheet #30 |
| ▪ Worksheet #15 | ▪ Worksheet #36 |
| ▪ Worksheet #16 | ▪ Worksheet #37 |

The CPG's QAPP and Field Sampling Plan provide procedures for the chemical water column low volume monitoring study.

1.1 Summary of Chemical Water Column Monitoring Sample Acceptance

CDM's oversight program is designed to provide technical review, verify the accuracy of the CPG's Chemical Water Column Monitoring (CWCM) study and evaluate the CPG-implemented QAPPs for sampling and analysis.

The CPG is performing the CWCM study to support fate and transport modeling and validation, exposure point calculations for the risk assessments, and assessing feasibility of remedial alternatives. The study will be conducted over the course of eight planned sampling events;

- Five Routine Events
- Two High flow Events
- One Low Flow/Spring Tide Event

CDM will accept split samples from CPG's contractor, AECOM. Split samples will be analyzed for select Groups A and B contaminants as requested by United States Environmental Protection Agency (EPA) and

United States Army Corps of Engineers (USACE) as follows:

- Polychlorinated biphenyl (PCB) congeners
- Polychlorodibenzodioxin/furan (PCDD/PCDF) congeners
- PAH and Alkylated PAH compounds
- Chlorinated pesticides
- Target analyte list (TAL) Metals (total and dissolved), and total titanium
- Total and dissolved mercury and methylmercury
- Hexavalent chromium (dissolved)
- Total dissolved solids (TDS)
- Total organic carbon (TOC)
- Dissolved organic carbon (DOC)
- Suspended solids concentration (SSC)/ total suspended solids (TSS)
- Particulate organic carbon (POC)

A subset of the TAL metals will be analyzed for the dissolved metals fraction (arsenic, cadmium, chromium, copper, lead, nickel, selenium, and zinc). Split samples will not be accepted for the following Group A and B analytes which will be analyzed by the CPG contractors: semi-volatile organic compounds (SVOCs), PCB Aroclors, cyanide, chlorophyll a, hardness (calculated), total Kjeldahl nitrogen (TKN), ammonia, total phosphorus and butyltins. This oversight QAPP details the planning and execution processes for accepting, preparing and shipping samples for analysis, and evaluation of the data.

QAPP Worksheet #1
Title and Approval Page

Document Title: LPR Restoration Project Final Quality Assurance Project Plan (QAPP) Addendum No. 8, Chemical Water Column Monitoring Study

Lead Organization: United States Army Corps of Engineers (USACE) – Northwestern Division

Preparer's Name and Organizational Affiliation: Jeniffer Oxford and Vanessa Macwan, CDM

Preparer's Address, Telephone Number, and E-mail Address: 14 Wall Street, Suite 1702
New York, NY 10005; (212) 377-4536; OxfordJM@cdm.com and 110 Fieldcrest Avenue, 6th Floor, Edison,
NJ 08837; (732) 590-4706; MacwanVC@cdm.com

Preparation Date (Day/Month/Year): August 2, 2011

Investigative Organization's Project Manager/Date:

Frank Tsang/CDM


Signature

Investigative Organization's Project QA Manager/Date:

Jo Nell Mullins/CDM


Signature

Lead Organization's Project Manager/Date:

Elizabeth Buckrucker/USACE – KC District

Signature

EPA Remedial Project Manager /Date:

Stephanie Vaughn

Signature

EPA Quality Assurance Officer /Date:

William Sy

Signature

Document Control Numbering System: Not Applicable (NA)

QAPP Worksheet #2
QAPP Identifying Information

Site Name/Project Name: Lower Passaic River (LPR) Restoration Project	Title: Final QAPP Addendum No. 8, Chemical Water Column Monitoring Study
Site Location: LPR study area, New Jersey	Revision Number: 1
Site Number/Code: NJD 980528996	Revision Date: NA
Operable Unit (OU): OU2	Contractor Name: Camp, Dresser, & McKee (CDM)
Contractor Number: W912DQ-08-D-0018	
Contract Title: Unrestricted Indefinite Delivery/Indefinite Quantity, Multiple Award Contract, for Architect-Engineer Environmental Services for EPA Region 2 and the Corps of Engineers Northwestern Division.	
Task Order Number: 14	

1. Regulatory program: Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (Superfund)
2. Approval entity: United States Army Corps of Engineers (USACE)
3. The QAPP is (select one): Generic ☒ **Project Specific**
4. Dates of negotiation: NA
5. Dates and titles of QAPP documents written for previous and current site work, if applicable:

Title	Approval Date
See Final QAPP for a full list of previous QAPP prepared for site work	
Lower Passaic River RI/FS Oversight Final QAPP, Physical Water Column Monitoring and Generic Information for Upcoming Tasks (PWCM/Generic QAPP) (referred to herein as Final QAPP)	March 2010
LPR RI/FS Oversight QAPP, Final Addendum No.1: <i>Avian Community Survey</i>	August 6, 2010
LPR RI/FS Oversight QAPP, Final Addendum No.2: <i>Fish Community Survey</i>	June 8, 2010
LPR RI/FS Oversight QAPP, Final Addendum No.3: <i>Benthic Invertebrate Community Survey</i>	June 8, 2010
LPR RI/FS Oversight QAPP, Addendum No.4: <i>Surface Sediment Sampling Co-located with the Small Forage Fish Tissue Samples during the Summer 2010 Benthic Community Survey oversight</i>	July 12, 2010
LPR RI/FS Oversight QAPP, Addendum No.5: <i>Fish Tissue Analysis</i>	August 24, 2010
LPR RI/FS Oversight QAPP, Addendum No.6: <i>Habitat Identification Survey</i>	August 9, 2010
LPR RI/FS Oversight QAPP, Addendum No.7: <i>Caged Bivalve Study</i>	April 29, 2011

6. Organizational partners (stakeholders) and connection with lead organization: United States Environmental Protection Agency (EPA), USACE, New Jersey Department of Environmental Protection (NJDEP), New Jersey Department of Transportation (NJDOT), National Oceanic Atmospheric Administration (NOAA), United States Fish and Wildlife Service (USFWS)
7. Data users: EPA, USACE, Partner Agencies, CDM, Louis Berger Group, Inc., HydroQual, Inc., and stakeholders
8. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusions below: the Final QAPP provides all the required worksheet not included herein. This addendum addresses only the Chemical Water Column Monitoring (CWCM) study; therefore, only worksheets pertinent to this task and information not previously provided are included.

**QAPP Worksheet #3
Distribution List**

QAPP Recipients	Title	Organization	Telephone Number	Fax Number	E-mail Address
Stephanie Vaughn	Remedial Project Manager (RPM)	EPA	(212) 637-4427	(212) 637-4393	vaughn.stephanie@epamail.epa.gov
Elizabeth Buckrucker	Project Manager (PM)	USACE	(816) 389-3581		elizabeth.a.buckrucker@usace.army.mil
William Sy	QA Officer	EPA	(732) 321-6648	(732) 321-6622	sy.william@epa.gov
Janine MacGregor	Partner Agency	NJDEP	(609) 633-0784		janine.macgregor@dep.state.nj.us
Elkins Green	Partner Agency	NJDOT	(609) 530-8075		elkins.green@dot.state.nj.us
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Frank Tsang	Project Manager	CDM	(212) 377-4056	(212) 785-6114	TsangC@cdm.com
Sharon Budney	Deputy Project Manager	CDM	(732) 590-4662	(732) 225-7851	BudneySL@cdm.com
Jeniffer Oxford or other assigned quality assurance coordinator (QAC)	Regional QA Coordinator / Project QA Officer	CDM	(212) 377-4536	(212) 785-6114	OxfordJM@cdm.com
George Molnar	Field Task Leader	CDM	(732) 590-4633	(732) 225-7851	MolnarGC@cdm.com
Scott Kirchner	Analytical Services Coordinator	CDM	(732)590-4677	(732) 225-7851	KirchnerSF@cdm.com
James Fitzpatrick	Sediment Transport Modeler	HydroQual	(201) 529-5151	(201) 529-5728	jfitzpatrick@hydroqual.com
Candice Navaroli	Laboratory Manager	Axys Analytical Services limited (Ltd.)	(250) 655-5800 or (888) 373-0881	TBD	cnavaroli@axys.com
John Birri	Laboratory Contact	DESA Laboratory	219-769-8378	(732) 906-6886	Birri.John@epamail.epa.gov
Nisreen Saikaly	Laboratory Project Manager	CDM Subcontract Laboratory-Shealy	(800) 673-9375 ext 106	(803) 791-9111	NSaikaly@Shealylab.com

QAPP Worksheet #9-a
Project Scoping Session Participants Sheet

Project Name: Small Volume Chemical Water Column Monitoring		Site Name: Lower Passaic River Restoration Project (LPR) RI/FS Oversight (OS)		
Projected Date(s) of Sampling: Summer 2011 and Spring 2011		Site Location: New Jersey		
Project Manager: Frank Tsang-CDM		Operable Unit: OU3		
Date of Session: November 4, 2010 and December 6, 2010				
Scoping Session Purpose: To discuss the CPG SOPs and appropriate oversight analytical methods for split samples and initiate coordination between oversight efforts in the Newark Bay Study Area by The Louis Berger Group, Inc. and oversight efforts on the Lower Passaic River by CDM.				
Name	Affiliation	Phone #	E-mail Address	Project Role
Eugenia Naranjo	EPA	212-637-3467	naranjo.eugenia@epa.gov	Project Manager – Newark Bay Study Area RI/FS
Alice Yeh	EPA	212-637-4427	yeh.alice@epa.gov	Project Manager – LPR RI/FS
Elizabeth Buckrucker	USACE	816-389-3581	Elizabeth.a.buckrucker@usace.army.mil	Project Manager
Len Warner	Louis Berger Group, Inc.	914-798-3721	lwagner@louisberger.com	Project Manager - Newark Bay Study Area OS
AmyMarie Accardi-Dey	Louis Berger Group, Inc.	914-798-3712	aacardidey@louisberger.com	Oversight Leader - Newark Bay Study Area OS
Sharon Budney	CDM	732-590-4662	budneysl@cdm.com	Deputy Project Manager – LPR OS
Scott Kirchner	CDM	732-590-4677	kirchnersf@cdm.com	Project Chemist/Data Manager
Jeniffer Oxford	CDM	212-377-4536	oxfordjm@cdm.com	Project Chemist

Comments/Decisions:

- Oversight will be conducted by The Louis Berger Group, Inc. in the Newark Bay Study Area and by CDM on the Lower Passaic River. Split samples collected by the two government contractors need to be collected consistently and analyzed following the sample analytical procedures to ensure consistency in the split sample dataset.
- The Louis Berger Group, Inc. and CDM will ship samples to the DESA laboratory and the Shealy and Axys subcontract laboratories consistent with CDMs Master Services Agreements. Advantages to this strategy are the minimization of sample volumes and consistency with data generation.
- A laboratory services request will be submitted to the DESA laboratory via RSCC to determine if they can perform the hexavalent chromium analysis.

Action Items:

CDM to send The Louis Berger Group, Inc. copies of the laboratory SOPs.

Complete coordination of analytical services.

CDM and The Louis Berger Group, Inc. will complete DESA analytical services request forms for the split sample program.

QAPP Worksheet #9-b
Project Scoping Session Participants Sheet

Project Name: Small Volume Chemical Water Column Monitoring Projected Date(s) of Sampling: Summer 2011 and Spring 2011 Project Manager: Frank Tsang-CDM			Site Name: Lower Passaic River Restoration Project (LPR) RI/FS Oversight (OS) Site Location: New Jersey Operable Unit: OU3	
Date of Session: May 5, 2011 Scoping Session Purpose: To discuss the CPG’s response-to-comments (dated April 15, 2011) on the SV CWCM QAPP and the oversight program.				
Name	Affiliation	Phone #	E-mail Address	Project Role
Eugenia Naranjo	EPA	212-637-3467	naranjo.eugenia@epa.gov	Project Manager – Newark Bay Study Area RI/FS
Alice Yeh	EPA	212-637-4427	yeh.alice@epa.gov	Project Manager – LPR RI/FS
Elizabeth Buckrucker	USACE	816-389-3581	Elizabeth.a.buckrucker@usace.army.mil	Project Manager
Len Warner	Louis Berger Group, Inc.	914-798-3721	lwerner@louisberger.com	Project Manager - Newark Bay Study Area OS
AmyMarie Accardi-Dey	Louis Berger Group, Inc.	914-798-3712	aacardidey@louisberger.com	Oversight Leader - Newark Bay Study Area OS
Edward Garland	HDR/ HydroQual, Inc.	201-529-5151	egarland@hydroqual.com	Modeler
Paul Paquin	HDR/ HydroQual, Inc.	201-529-5151	ppaquin@hydroqual.com	Modeler
Sharon Budney	CDM	732-590-4662	budneysl@cdm.com	Deputy Project Manager – LPR OS
Scott Kirchner	CDM	732-590-4677	kirchnersf@cdm.com	Project Chemist/Data Manager

Comments/Decisions:

- CPG's proposal to conduct the SV CWCM program as described in the CPG SV CWCM QAPP will be approved. This includes the collection and analysis of 1-liter whole water samples for organic parameters
- Event 1 of the Routine sampling event will test the small-volume (SV), whole-water analytical methods. CPG will submit at least 20 samples located in Newark Bay or the Lower Passaic River for rapid analytical turnaround of the Group A parameters. These 20 samples will be collected from EPA pre-selected locations to test the low-end sensitivity of the SV analytical methods. The quick turnaround analysis of select parent and split samples from the initial sampling event will facilitate review by EPA, CPG, and TSI and a final decision on the efficacy of the SV CWCM program made by EPA. Adjustments to the SV sampling and analytical methods will then be made as needed based on the review of the quick turnaround data. The effectiveness of the SV sampling will be determined by EPA prior to the continuation of the remainder of the SV CWCM program.
- Split samples will follow the SV, whole water analytical procedures outlined in the CPG SV CWCM QAPP. The Louis Berger Group, Inc. recommended the collection of a subset of large volume, co-located samples in addition to the split samples to test the sensitivity of the 1-liter, whole water methodology; however, EPA directed The Louis Berger Group, Inc. and CDM to collect split samples only and to follow the CPG's proposed analytical procedures.
- Split samples will target the EPA pre-selected 20 locations with a rapid analytical turnaround of Group A parameters (other split samples will be shipped with regular turnaround).

Action Items:

CDM will prepare an oversight QAPP for the small volume CWCM Study.

Follow up Post Scoping Meeting:

LBG and CDM will share responsibility for providing PE samples to the subcontract laboratories by alternating that responsibility by alternating delivery of the PE for each event to a maximum of 1 per quarter. CDM will be responsible for the PEs for the initial sampling event scheduled for mid August and LBG will provide PE coverage for the next event and so on.

QAPP Worksheet #10
Problem Definition

The problem to be addressed by the project:

The Cooperating Parties Group (CPG) is conducting a study of the Lower Passaic River and the Newark Bay Study Areas to provide data needed to characterize chemical concentrations in the water column. This data will support the risk assessments and the chemical fate and transport model. CDM will provide oversight and analysis of split samples collected from the LPR Study Area to verify the CPG's compliance with their approved project plans and accuracy of the derived data. The Louis Berger group will provide oversight and analysis of split samples collected from the Newark Bay Study Area.

Oversight will include:

- Technical Review and evaluation of CPG's project plans
 - Documentation of field activities observations and deficiencies
 - Acceptance of split water samples
 - Sample handling, packaging and shipping to off-site laboratories
 - Review of CPG-selected sampling locations
 - Comparison of the data sets to determine any analytical bias
- Additional information is provided on Worksheet 11.

The environmental questions being asked:

- Is the CPG contractor complying with the approved plans?
- Does the CPG data adequately describe the site conditions and is it representative for project decisions?
- Are the CPG and CDM data complete and accurate?
- Are the data sets comparable?
- Does the data show any analytical bias?
- Are the relative percent differences (RPDs) between the CPG and CDM data within the measurement performance criteria?

Secondary data: See Worksheet 13 of the CPG QAPP (AECOM 2011)

The possible classes of contaminants and the affected matrices:

Split surface water samples will be collected for the following chemical analyses:

- Polychlorinated biphenyl (PCB) congeners
- Polychlorodibenzodioxin/furan (PCDD/PCDF)

QAPP Worksheet #10
Problem Definition

- Polyaromatic hydrocarbons (PAH) and Alkylated PAH compounds
- Chlorinated pesticides
- Target analyte list (TAL) Metals (total), total titanium, and dissolved metals (arsenic, cadmium, chromium, copper, lead, nickel, selenium, and zinc)
- Total and dissolved mercury and methylmercury
- Hexavalent chromium (dissolved)
- Total dissolved solids (TDS)
- Total organic carbon (TOC)
- Dissolved organic carbon (DOC)
- Suspended solids concentration (SSC)
- Particulate organic carbon (POC)

Split samples will not be accepted for the following analytes which will be analyzed by the CPG contractors: semivolatile organic compounds (SVOCs), PCB Aroclors, cyanide, chlorophyll a, hardness (calculated), total Kjeldahl nitrogen (TKN), ammonia, total phosphorus and butyltins.

The rationale for inclusion of chemical and non-chemical analyses:

The split samples will be used to support the goals of the oversight program. The split sample analyses were determined to be more critical for oversight evaluation; the analyses that will not be split are ancillary parameters and not major risk drivers. The field observations and split sample data will enable CDM to perform technical review and evaluation on the CPG field program, analytical data and reports and to assess any potential bias in the CPG dataset.

Project decision conditions (“If..., then...” statements):

- If sample results are not comparable with the CPGs, then CDM will note deviations in the Data Reports submitted to USACE and EPA. The CDM Project Manager, USACE PM and EPA RPM will be informed if there are deviations.
- If the CPG team needs to relocate survey locations, reprioritize analytical parameters, or if there are any changes to the planned analytical program, CDM will communicate this change to the USACE and EPA and document it in the Data Reports.

CDM will present the data findings in a Data Report and submit it to the USACE and EPA who will then determine if any additional actions are required.

QAPP Worksheet #11
Project Quality Objectives /Systematic Planning Process Statements

Who Will Use the Data? USACE, EPA and other partner agencies, CDM, and stakeholders (as necessary).

What Will the Data be Used For?

The CPG will use the study to characterize chemical concentrations in the water column. This data will support the risk assessments and the chemical fate and transport model of the LPRSA. Oversight activities will monitor the CPG-implemented study, sampling, and analytical program to verify that elements of the approved RI/FS QAPPs are fulfilled. The CDM field crew will also review the CPG-selected sampling locations and procedures. CDM's split sample results will be compared to the data obtained by the CPG to determine if a bias exists in the data produced by the CPG and if the data are complete, accurate and compliant with the approved QAPPs.

A comparison of the split sample data and the CPG parent sample data will only be completed for parameters that were analyzed and detected by both the CPG program and the oversight program. Data comparison will not be conducted on concentrations that are non-detect. (Note that if a consistent bias in detections is observed in either the split samples or CPG samples, an evaluation of detection limits will be completed.) The data comparison will be presented in a table showing the relative percent difference for values that are 5 times the quantitation limits. As appropriate, alternative data comparisons will be provided. For each location, a mean and variance of the sample concentrations may also be calculated. These statistics will be compared to the CPG samples. For analytical groups that contain multiple parameters (e.g., congeners), the data comparison will be completed on select parameters per chemical class. Parameters will be selected by the project chemist/and analytical service coordinator to cover a range of concentrations from non-detects to high concentrations. In addition analytes of greater risk or of greater concern will be selected for comparison over other analytes. This selection will be made with the consensus of the USACE and EPA.

CDM's quality control (QC) data will be used to determine CDM's split sample data quality and comparability with the CPG's data and whether sample results are acceptable based on the established project data quality objectives (DQOs). QC sample results will be compared to the measurement performance criteria (MPC) of the data quality indicators (DQIs).

To further achieve these objectives, CDM field personnel will observe and monitor the CPG contractor's implementation of the RI/FS QAPPs and will note any deviations. Deviations will be brought to the attention of the CPG's contractor, and reported to the CDM project manager who will communicate this information to the USACE PM and EPA RPM. These will be documented in ongoing and Final Reports and include a discussion of the impact of the deviation(s) on the data quality. The CPG contractor's activities will be documented in the field logbook and oversight forms. A copy of the oversight form is provided in Appendix B of CDM's Final QAPP.

What Type of Data is Needed?

Split water column samples will be collected at locations and depths selected by mutual agreement between CDM and the CPG contractor or as directed by the CDM Deputy PM or the USACE/EPA project managers.

Chemical data will be obtained from the split samples accepted from the CPG. Low limits are required for mercury and methylmercury and organic parameters as shown on QAPP worksheet #15.

QAPP Worksheet #11
Project Quality Objectives /Systematic Planning Process Statements

How much data are needed?

CDM will accept split samples at approximately 10 percent of the sampling locations. Worksheets #11 and 18 of the CPG's CWCM QAPP and Figure 1 show the planned locations for sampling.

Approximately 10 percent of the samples will be split to determine if a bias exists in the data produced by the CPG. Field rinsate blanks will also be sent for analysis. Oversight activities are listed in Worksheet 10. Field duplicates will be analyzed for each sample event. Performance evaluation (PE) samples will also be obtained and submitted. CDM will alternate the use and analysis of PE samples for alternate sampling events with the Louis Berger Group.

How "good" do the data need to be in order to support the environmental decision?

Definitive level data are required to produce the data quality required for risk assessments, full validation of the data and to enable comparison with the CPG generated data set. Fixed based laboratories with EPA, Environmental Laboratory Accreditation Program or national Environmental Laboratory Accreditation Program certifications and qualification will be used to generate the analytical data. CDM has attempted to use comparable methods and obtain similar reporting limits to the CPG's. CDM's oversight staff will document whether the in CWCM study is in compliance with the CPG's QAPP. The representativeness of the data is dependent on the sampling design established by the CPG. Split samples will be obtained by the alternate filling of the sample bottles with the CPG's contractor with a sufficient volume to fulfill analytical needs.

The laboratory reporting limits (contract required quantitation limits (CRQLs)) for DESA data, or reporting limits for subcontract laboratory data), need to be below or equal to the CPG's project required quantitation limits goals or the CPG's achievable laboratory quantitation limits. CDM will notify EPA's Regional Sample Control Coordinator (RSCC) or the subcontract laboratory and request lower reporting limits to achieve the project data quality objectives for sensitivity as needed.

Validation of data will be performed by Division of Environmental Science and Assessment (DESA)/ EPA; however, samples analyzed by a subcontract laboratory will be validated by CDM.

In addition, to ensure that measurement performance criteria for usability (criteria for DQIs) are met, all CDM data will be subject to a data usability assessment. The inputs will be the EPA generated validation reports and CDM's data validation summary reports. Measurement performance criteria presented in Worksheets No.12, 28, 35 and 36 will be evaluated as discussed on Worksheet No.37. The results will be presented in a CDM data report.

The data usability assessment will evaluate whether appropriate field procedures were followed and whether data met the approved QAPP and project DQOs, and are usable for the stated project needs.

QAPP Worksheet #11
Project Quality Objectives /Systematic Planning Process Statements

Where, when, and how should the data be collected?

When – Split surface water samples will be accepted from the CPG’s contractor laboratory. The CPG’s contractor will collect the samples between early summer 2011 and summer 2012, the surface water collection events are shown in the table below excerpted from the CPG’s QAPP. This CWCM survey will be performed according to the CPG’s schedule. The exact sampling dates are to be determined.

Where – The surface water will be collected from the LPRSA locations shown on Figure 1 including River Mile 0. CPG’s QAPP worksheet 11 describes the flow conditions under which certain locations will be sampled. Pre-selected locations will be submitted for rapid analytical turnaround of Group A parameters; all other locations will be sent for regular turnaround of results. All split locations will be determined by the CDM field oversight personnel in consultation with the CDM deputy project manager and EPA.

How – Sampling procedures are described in the CPG’s QAPP (AECOM 2011) (various worksheets) and the CPG’s Field Sampling Plan and its Attachment B. Split samples will be facilitated by the use of an in-line splitter allow simultaneous collection of samples by the CPG’s contractor and CDM.

Sampling Event Type	Season/ Frequency	Analyte Groups	
		A	B
Routine Events*	One in Winter Two in Spring Two in Summer	All 8 Events	One in Spring Two in Summer
High Flow Events	As encountered		One event
Low Flow/ Spring Tide Event	One in late Summer/ One in early Fall		One event

*One routine event will spring tide conditions and one will target neap tide conditions.

Who will collect and generate the data?

CDM oversight staff will record field observations in logbooks and on the Field Oversight Form in Appendix O. The CPG’s contractor will provide a split a portion of the water samples to CDM who will label, pack and ship to the appropriate laboratory. The CPG’ contractor will filter samples for dissolved analysis and use a splitter in the sample tubing after the in-line filter to provide split samples for dissolved analysis. The analytical laboratories outlined in this Final QAPP Addendum will generate the data.

QAPP Worksheet #11
Project Quality Objectives /Systematic Planning Process Statements

How will the data be reported?

- Accepted split samples will be recorded as described in CDM's Final QAPP using field logbooks in accordance with technical standard operating procedure (TSOP) 4-1 provided in Appendix C of the Final QAPP.
- Results will be reported in text format and will include a discussion of the data quality, deviations from the QAPP, and oversight data comparability with the CPGs data. This review will be used to evaluate the accuracy of the CPG data.
- Sample results generated by the DESA laboratory will be e-mailed to CDM for use in the data assessment and evaluation
- Sample results generated by CDM's subcontract laboratory will be e-mailed to CDM for review and validation.
- Data reporting is further covered in the Final QAPP.

How will the data be archived?

- Hard copies of data will be kept in the CDM Edison office until archived in the project file; if requested, survey data will be uploaded to the EarthSoft Environmental Quality Information System (EQulS) database.
- The Final QAPP contains other archival information.

QAPP Worksheet #12-a
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group ^a	PAH and Alkyl PAHs				
Concentration Level	Low				
Sampling Procedure	Analytical Method/ standard operating procedure (SOP)	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC) ¹	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
CPG Group’s SOP, and QAPP (LPR-FI-04)	Axys SOP MLA-021	Accuracy/Bias-Contamination	No target compound > quantitation limit (QL)	Method Blank /Instrument Blank	A
		Accuracy/Bias-Contamination	No target compound >QL	Equipment Rinsate Blank	S & A
		Accuracy/Bias	Per laboratory SOP	Ongoing Precision and Recovery (OPR) / Certified Reference Material	A
		Accuracy/Bias	50-150 percent (%)	Matrix spike (MS)	A
		Accuracy/Representativeness	4±2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks DV	S & A
		Accuracy/Bias	RPD ≤ 20% for concentrations > 10x detection limit (DL) ²	Laboratory Duplicate	A
		Accuracy/Bias	15-130% recovery (R) Axys	Surrogate	A
		Accuracy/Bias	Supplier Certified Limits	PE Sample Data Review or Sample Analysis ^b	A
		Comparability	Comparable units, and methods	Evaluated during DQA	S & A
		Precision	RPD ≤40% if both samples are >5x QL or absolute difference (ABS) <2x QL if either result is ≤5x QL	Splits and Field Duplicate	S & A
		Completeness	≥90%	Data Completeness Check data quality assessment (DQA)	S & A

Notes:

- Refer to QAPP Worksheet #15 for a complete list of analytes for each analytical group
 - The PE program will include a review of existing PE results; a project-specific PE sample will be analyzed in the event that historical data are not adequate to assess laboratory performance for the matrix/method combinations planned for the CWCM, or where deficiencies were noted in the existing PE data. Refer to Worksheets #28 and #31 for additional details of the program.
- The Measurement Performance Criteria are derived from the laboratory SOPs. The laboratory must perform and meet all the quality assurance requirements specified in the laboratory method SOP.
 - CDM will check if the DLs referenced in the laboratory SOP are equivalent to the MDLs or the quantitation limits and clarify the term accordingly in the next revision.

QAPP Worksheet #12-b
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	Chlorinated Pesticides				
Concentration Level	Low				
Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	EPA Method 1613B Modified Axys Lab SOP MLA-035 R06 Method is proprietary; a summary of MSU—035 is provided in Appendix M HRGC/HRMS	Precision	RPD \leq 40% if concentration \geq 5 QL	Split samples and field duplicates	S & A
		Precision	\pm 40% if concentration $>$ 10DL ²	Laboratory duplicate	A
		Accuracy/Bias	50-150%	LCS	A
		Accuracy/Bias	Supplier Certified Limits Per laboratory or method SOP \pm 20%	Certified Reference Material (CRM) Calibration Verification	A
		Accuracy/Bias	50-130% recoveries or per SOP MLA-035	OPR (LCS)/Matrix Spike	A
		Accuracy/Representativeness	4 \pm 2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S
		Accuracy/Bias	30-200% recovery (See SOP for individual limits)	Surrogate	A
		Comparability	Comparable units, and methods	Evaluated during DQA	S & A
		Completeness	\geq 90% Collection and \geq 90% Valid data	Evaluated during DQA	S & A
		Sensitivity/accuracy	\leq QLs (WS#15 and laboratory SOP)	Field rinsate/ Method blanks assessed during DV and DQA	S & A

Notes:

1. The laboratory must perform and meet all the quality assurance requirements specified in MLA-035 including: performance of initial and ongoing studies, calibration verification, addition of internal standards, analyses of blanks and determination of detection limits.
2. The DLs referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits.

QAPP Worksheet #12-c
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	PCB Congeners				
Concentration Level	Low				
Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria¹ (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept splits	EPA Method 1668B AXYS Laboratory MLA-010 Revision 10	Precision	RPD \leq 40% if concentration \geq 5 CRQL	Split samples and field duplicates	S & A
		Precision	\pm 20% of mean if concentration $>$ 10DL ²	Laboratory duplicate	A
		Accuracy/Bias	Supplier Certified Limits 70 -130 %recovery	CRM; Calibration Verification Sample	A
		Accuracy/Bias Precision	60-140 %recovery RSD \leq 40%	Initial Precision and Recovery	A
		Accuracy/Bias	Per laboratory SOP Warning 70-130%R; Accept 50-150 %recovery	LCS or OPR	A
		Accuracy/ Representativeness	4 \pm 2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks DV	S
		Comparability	Comparable units, and methods	Assessed during DQA	S & A
		Completeness	\geq 90% collection and analysis	Assessed during DQA	S & A
		Sensitivity/ accuracy	\leq QLs (WS#15 and laboratory SOP)	Field rinsate/ Method blanks assessed during DV and DQA	S & A

Notes:

1. The assigned laboratory must perform and meet all the quality assurance requirements specified in the method.
2. The DLs referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits.

QAPP Worksheet #12-d
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	PCDD/PCDF				
Concentration Level	Low				
Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)¹	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	USEPA Method 1613B – Axys Analytical Services SOP MSU-018 Method is proprietary; a summary is provided in Appendix M	Precision	RPD \leq 40% if concentration \geq 5 QL	Split samples and field duplicates	S & A
		Precision	\pm 20% of mean if concentration $>$ 10DL ²	Laboratory duplicate	A
		Accuracy/Bias	70-130 %recovery (or per laboratory SOP)	MS/MSD	S & A
		Precision	RPD \leq 20%		
		Accuracy/Representativeness	4 \pm 2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks DV	S
		Precision	Per laboratory SOP	Initial precision and recovery standard	A
		Accuracy/Bias	Various % recovery per laboratory SOP		
		Accuracy/Bias	70-130 %recovery	OPR	A
		Accuracy/Bias	21-130% recovery	Surrogate standards	A
		Comparability	Comparable units, and methods	Evaluated during DQA	S & A
		Completeness	\geq 90% collection and analysis	Evaluated during DQA	S & A
		Sensitivity/accuracy	\leq QLs (WS#15 and laboratory SOP)	Field rinsate/ Method blanks assessed during DV and DQA	S & A

Notes:

1. The assigned laboratory must perform and meet all the quality assurance requirements specified in the method.
2. The DLs referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits.

QAPP Worksheet #12-e
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	Total and Dissolved Metals (no Mercury)				
Concentration Level	Low				
Sampling Procedure	Analytical Method/SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC) ¹	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	SW-846 Method 6020 ICP-MS Shealy SOP S-IM-021; 6020, Revision 2	Precision	RPD \leq 40% if concentration \geq 5 CRQL	Split samples and field duplicates	S & A
		Precision	RPD \leq 20%	Laboratory duplicate	A
		Accuracy/Bias	80-120 %recovery 75-125 %recovery	LCS; MS	A
		Accuracy/Representativeness	4 \pm 2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks DV	S & A
		Comparability	Comparable units, and methods	Evaluated during DQA	S & A
		Completeness	\geq 90% Collection and \geq 90% Valid data	Evaluated during DQA	S & A
		Sensitivity/accuracy	\leq CRQLs (WS#15)	Field rinsate/ Method blanks assessed during DV and DQA	S & A

Notes:

1. The assigned laboratory must perform and meet all the quality assurance requirements specified in their method SOP.

QAPP Worksheet #12-f
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	Total and Dissolved Mercury				
Concentration Level	Trace (nanogram per liter (ng/L))				
Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)¹	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	EPA Method – 1631 Microbac SOP Hg-1631, Revision 2	Precision	RPD \leq 40% if concentration \geq 5 CRQL	Split samples and field duplicates	S & A
		Accuracy	RPD \leq 25% for values \geq 10 method detection limit (MDL). No more than 35% of RSDs $>$ 25%	Laboratory duplicate	A
		Accuracy/Bias	70-130 %recovery	MS/MSD	A
		Precision	Laboratory SOP or RPD \leq 30-35%; RSDs $<$ 20%	MS/MSD; Initial Precision and Recovery	A
		Accuracy	Laboratory SOP or 70-130%R; 75-125%R	OPR; Standard Reference Material	A
		Accuracy/ Representativeness	4 \pm 2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks DV	S & A
		Comparability	Comparable units, and methods	Evaluated during DQA	S & A
		Completeness	\geq 90% Collection and \geq 90% Valid data	Evaluated during DQA	S & A
		Sensitivity/ accuracy	\leq QLs (WS#15 and laboratory SOP) \leq 5MDLs	Field rinsate/ Method blanks assessed during DV and DQA	S & A

Notes:

The assigned laboratory must perform and meet all the quality assurance requirements specified in their method SOP.

QAPP Worksheet #12-g
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	Methyl mercury				
Concentration Level	Trace				
Sampling Procedure	Analytical Method/ SOP	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)¹	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP CDM will accept split	EPA Method – 1630 Microbac SOP Methyl Mercury Draft, Revision 0	Precision	RPD \leq 40% if concentration \geq 5 CRQL	Split samples and field duplicates	S & A
		Accuracy	RPD \leq 35% for values \geq 5 MDL. No more than 35% of RSDs $>$ 35%	Laboratory duplicate	A
		Accuracy/Bias	65-135 %recovery	MS/MSD	A
		Precision	RPD \leq 35%	MS/MSD	A
		Accuracy	67-133%R of certified value	Ongoing Precision and Recovery (Standard Reference Material)	A
		Accuracy/Representativeness	4 \pm 2 degrees Celsius 10 degrees Celsius (DV)	Temperature Blank checks Data validation (DV)	S & A
		Comparability	Comparable units, and methods	Evaluated during DQA	S & A
		Completeness	\geq 90% Collection and \geq 90% Valid data	Evaluated during DQA	S & A
		Sensitivity/accuracy	\leq QLs (WS #15) \leq 5 MDLs	Field rinsate/ Method blanks assessed during DV and DQA	S & A

Notes:

The assigned laboratory must perform and meet all the quality assurance requirements specified in their method SOP.

QAPP Worksheet #12-h
Measurement Performance Criteria Table

Matrix	Aqueous - dissolved				
Analytical Group	Hexavalent Chromium				
Concentration Level	Colorimetric/ Low				
Sampling Procedure¹	Analytical Method/SOP²	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)¹	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
¹ Refer to QAPP Worksheet #21	Hexavalent Chromium-218.6 (DESA SOP TBD) or Standard Method (SM) 3500 Cr-B and HACH 8023 Modified (DESA SOP C-96)	Precision	RPD ≤ 40% if concentration ≥ 5 QL	Sample splits and Field Duplicate ³	S & A
		Accuracy	No analyte > QL*	Field Equipment Blank	S & A
		Accuracy/Representativeness	≤ 10 degrees Celsius	Temperature Blank	S
		Precision	≤ 20% RPD* ABS ≤ QL	Laboratory Duplicate	A
		Accuracy	85-115% R or as updated by laboratory	Quality Control Sample (QCS); Laboratory Fortified Blank /DV	A
		Sensitivity	No analyte > QL* Detection limits meet project goals	Method Blank Sample specific non-detections	A
		Accuracy	80-120% recovery	Matrix Spike	A
		Completeness	≥ 90%	Data Assessment	S & A
		Comparability	Similar Units (µg/L) and methods	Data Review	S & A

Notes:

¹ The laboratory must perform and meet all the quality assurance requirements specified in the laboratory method SOP.

² If a subcontract laboratory is utilized, the laboratory will provide the SOP as part of the procurement.

³ RPDs (relative percent difference) will be determined for all detected results >5*QL. The absolute difference (ABS) will be calculated for any results reported below five times the quantitation limit (QL).

*Refer to Worksheet 15 for the required quantitation limits.

QAPP Worksheet #12-i
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	Total Suspended Solids				
Concentration Level	Low				
Sampling Procedure	Analytical Method/ SOP¹	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)^{1,4}	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP	SM2540D (DESA SOP C-37 Modified) ²	Precision	RPD \leq 40% if values $>5 \times \text{QL}$; otherwise $\text{ABS} \leq \text{QL}$	Field duplicates	S & A
		Precision	See worksheet #11	Split samples	S & A
		Accuracy/Bias	80-120%R or as stipulated by manufacturer or laboratory	Quality Control Sample (QCS) or Laboratory Fortified Blank	A
		Accuracy/Representativeness	4 \pm 2 degrees Celsius 10 degrees Celsius for DV ³	Temperature Blank checks DV	S
		Precision	$\leq 20\%$ RPD if values $>5 \times \text{QL}$; otherwise $\text{ABS} \leq \text{QL}$	Laboratory matrix duplicate/ DV ³	A
		Comparability	Comparable units, QLs and methods	Data Quality assessment	S & A
		Completeness	$\geq 90\%$	Data Quality Assessment	S & A
		Sensitivity/accuracy	$\leq \text{QLs}^3$	Method blanks	A
		Sensitivity	Detection limits meet project goals	Data Review	A

Notes:

1. The laboratory must perform and meet all the quality assurance requirements specified in the laboratory method SOP.
2. QAPP Worksheet # 23 provides more information on the sampling and analytical SOPs. Method SM 2540D is equivalent to American Society of Testing and Materials (ASTM) 3977-97 Test Option B.
3. QAPP worksheet #36 describes the data validation procedures to be used. The data validator will check to verify if the MPC are met.
4. See worksheet #15 for the QL requirements.

QAPP Worksheet #12-j
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	Wet Chemistry				
Concentration Level	Low [Carbon Converter + Infra-red or Flame Ionization Detector]				
Sampling Procedure¹	Analytical Method/SOP²	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
¹ Refer to QAPP Worksheet #21	Total Organic Carbon (TOC) – SM5310B, DESA SOP C-83	Precision	RPD ≤ 40% if values >5xQL; otherwise ABS ≤ QL	Sample Splits and Field Duplicate ³	S & A
		Accuracy/Representativeness	≤ 10 degrees Celsius	Temperature Blank	S
		Precision	≤ 20% RPD for samples >5xQL; ± QL for samples <5xQL*	Duplicate Sample	A
		Accuracy	75–125%; 80–120 % recovery	Matrix Spike; LCS	A
		Sensitivity	≤ QL	Method Blank	A
		Completeness	≥ 90%	Data Assessment	S & A
		Comparability	Similar Units (µg/L) Detection limits meet project goals	Data Review	S & A

Notes:

1. The laboratory must perform and meet all the quality assurance requirements specified in the laboratory method SOP.

² If a subcontract laboratory is utilized, the laboratory will provide the SOP as part of the procurement. DESA's updated SOPs will be included with the updated QAPP.

³ RPDs (relative percent difference) will be determined for all detected results.

*Refer to Worksheet 15 for the required quantitation limits.

QAPP Worksheet #12-k
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	Dissolved Organic Carbon (DOC)				
Concentration Level	Low				
Sampling Procedure	Analytical Method/ SOP ¹	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP	Laboratory Filtration + SM 5310B (DESA SOP C-83 Modified)	Precision	RPD \leq 40% if values $>5x$ QL; otherwise ABS $< 5x$ QL	Field duplicates and Split samples	S & A
		Accuracy	80-120%R	Matrix Spike	A
		Accuracy/Bias	80-120%R or as updated by laboratory or stipulated by manufacturer	Quality Control Sample (QCS); Laboratory Fortified Blank /DV	A
		Precision	RPD \leq 20% if values $>5x$ QL; otherwise ABS $< 5x$ QL	Laboratory replicate	
		Accuracy	85-115%R	Initial calibration verification (ICV)/ continue calibration verification (CCV)	A
		Accuracy/ Representativeness	4 \pm 2 degrees Celsius 10 degrees Celsius for DV ³	Temperature Blank checks Data validation /DV	S & A
		Comparability	Comparable units, QLs and methods	Data Quality assessment	S & A
		Completeness	\geq 90%	Data Quality Assessment	S & A
		Sensitivity/ accuracy	\leq QLs ⁴	Method blanks/Calibration Blank	A
		Sensitivity	Detection limits meet project goals	Data Quality Assessment	A

Notes:

1. The laboratory must perform and meet all the quality assurance requirements specified in the laboratory method SOP.
2. QAPP Worksheet # 23 provides more information on the sampling and analytical SOPs.
3. QAPP worksheet #36 describes the data validation procedures to be used. The data validator will check to verify if the MPC are met.
4. See worksheet #15 for the QL requirements.

QAPP Worksheet #12-I
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	Particulate Organic Carbon (POC)				
Concentration Level	Low				
Sampling Procedure	Analytical Method/ SOP¹	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC)	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP	Laboratory Filtration + EPA 415.1 (DESA SOP C-88 Modified)	Precision	RPD \leq 40% if values $>5 \times \text{QL}$; otherwise $\text{ABS} \leq \text{QL}$	Field duplicates	S & A
		Precision	See worksheet #11	Split samples	S & A
		Accuracy/Bias	80-120%R or as stipulated by manufacturer or laboratory	Quality Control Sample (QCS) or Laboratory Fortified Blank or Standard Reference Material	A
		Precision	$\leq 20\%$ RPD		
		Precision	$\leq 20\%$ RPD if values $>5 \times \text{QL}$; otherwise $\text{ABS} \leq \text{QL}$	Laboratory matrix duplicate/ DV ³	A
		Accuracy	85-115%R	ICV/CCV	A
		Accuracy/ Representativeness	4 \pm 2 degrees Celsius 10 degrees Celsius for DV ²	Temperature Blank checks Data validation /DV	S
		Comparability	Comparable units, QLs and methods	Data Quality assessment	S & A
		Completeness	$\geq 90\%$	Data Quality Assessment	S & A
		Sensitivity/ Accuracy	$\leq \text{QLs}^4$	Method blanks/Calibration Blank	A
			Detection limits meet project goals	Data Quality Assessment	A

Notes:

1. The laboratory must perform and meet all the quality assurance requirements specified in the laboratory method SOP.
2. QAPP Worksheet # 23 provides more information on the sampling and analytical SOPs. Method 415.1 is equivalent to EPA 440.0.
3. QAPP worksheet #36 describes the data validation procedures to be used. The data validator will check to verify if the MPC are met.
4. See worksheet #15 for the QL requirements.

QAPP Worksheet #12-m
Measurement Performance Criteria Table

Matrix	Aqueous				
Analytical Group	Suspended Solids Concentration (SSC)				
Concentration Level	Low				
Sampling Procedure	Analytical Method/ SOP ¹	Data Quality Indicators (DQIs)	Measurement Performance Criteria (MPC) ⁴	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or Both (S&A)
CPG Group's SOP, and QAPP	SM 2540D/E (DESA C-33 Modified) ²	Precision	RPD \leq 40% if values $>5 \times \text{QL}$; otherwise $\text{ABS} \leq \text{QL}$	Field duplicates	S & A
		Precision	See worksheet #11	Split samples	S & A
		Accuracy/Bias	80-120%R or as stipulated by manufacturer or laboratory	Quality Control Sample (QCS) or Laboratory Fortified Blank	A
		Accuracy/Representativeness	4 \pm 2 degrees Celsius 10 degrees Celsius for DV ³	Temperature Blank checks Data validation (DV)	S
		Precision	$\leq 20\%$ RPD if values $>5 \times \text{QL}$; otherwise $\text{ABS} \leq \text{QL}$	Laboratory matrix duplicate/ DV ³	A
		Comparability	Comparable units, QLs and methods	Data Quality assessment	S & A
		Completeness	$\geq 90\%$	Data Quality Assessment	S & A
		Sensitivity/Accuracy	$\leq \text{QLs}^3$	Method blanks	A
		Sensitivity	Detection limits meet project goals	Data Review	A

Notes:

1. The laboratory must perform and meet all the quality assurance requirements specified in the laboratory method SOP.
2. Method SM 2540D is equivalent to ASTM 3977-97 Test Option B.
3. QAPP worksheet #36 describes the data validation procedures to be used. The data validator will check to verify if the MPC are met.
4. See worksheet #15 for the QL requirements.

QAPP Worksheet #14
Summary of Project Tasks

Sampling Tasks:

CDM will accept split samples from the CPG's sampling contractor during each CWCM study sampling event. CDM's oversight staff will package, label and ship samples and QC samples to the DESA laboratory and the subcontract laboratories outlined on QAPP Worksheet 30.

Analysis Tasks:

Split samples will be collected from the CWCM study.

Analyses of surface water samples will include PAHs, Alkyl PAHs, chlorinated pesticides, PCB congeners, PCDD/PCDF, metals (total and dissolved), mercury (total and dissolved), methylmercury (total and dissolved), dissolved hexavalent chromium, TDS, TOC, DOC, POC, and SSC.

Quality Control Tasks: CDM will observe CPG's sampling of the surface water samples. CDM will accept splits and one field rinsate blank of the equipment used to collect the samples. Field duplicate samples will be collected as outlined on Worksheet #20. PE sample may be collected for at least one sampling event or alternately with the Louis Berger Group. The CDM Deputy Project Manager or designee will review the logs to ensure that the required information has been documented.

Secondary Data: Since this is an oversight project, no secondary data are being used directly by CDM. Data generated by the CPG - field program will be used as shown on worksheet 11 of the CPG's Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection QAPP.

Data Management Tasks:

Analytical data generated by the various laboratories will be managed according to the procedures described in the Final QAPP.

Documentation and Records: Records of accepted surface water samples will be documented in accordance with TSOP 4-1 provided in Appendix C of the Final QAPP. The Surface water analysis results will be documented in the following:

1. Data Validation reports
2. Chain of custody (COCs), Analytical Services Tracking System (ANSETS), and Trip Report
3. Oversight summary report
4. Data Quality and Usability Summary Report

Assessment/Audit Tasks: See Final QAPP for assessment tasks (CDM 2009)

Data Review Tasks: The CPG's Data Summary Report will be reviewed by CDM. A data quality evaluation will be performed based on the CPG's compliance with their approved QAPP. A comparison of CDM's and the CPG's surface water sample results will be included in the data quality evaluation and submitted to the USACE.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous

Analytical Group: PAH and Alkyl PAHs by Axys Laboratory SOP: MLA-021 R09

Concentration Level: Low (µg/L = microgram per liter)

Analyte	CAS Number	Project Action Limit ¹ (PAL)	Project Quantitation Limit Goal ² (PQLG)	Analytical Method ³		Achievable Laboratory Limits ³	
				MDLs	8270 QL	MDLs	QLs
1-Methylnaphthalene	90-12-0	2.10E+00	1.00E-02	NA	Not Listed	NA	0.01
1-Methylphenanthrene	832-69-9	1.10E+03	1.00E-02	NA	Not Listed	0.0012	0.01
2,3,5-Trimethylnaphthalene	2245-38-7	1.40E-01	1.00E-02	NA	Not Listed	0.0052	0.01
2,6-Dimethylnaphthalene	581-42-0	1.40E-01	1.00E-02	NA	Not Listed	0.0015	0.01
2-Methylnaphthalene	91-57-6	1.50E+01	2.00E-02	NA	10	0.0018	0.01
Acenaphthene	83-32-9	2.20E+02	1.00E-02	NA	10	0.0018	0.005
Acenaphthylene	208-96-8	2.20E+02	1.00E-02	NA	10	0.0014	0.005
Anthracene	120-12-7	7.30E-01	1.00E-02	NA	10	0.0037	0.005
Benzo[a]anthracene	56-55-3	3.80E-03	1.00E-02	NA	10	0.0013	0.005
Benzo[a]pyrene	50-32-8	2.90E-03	1.00E-02	NA	10	0.0013	0.005
Benzo[b]fluoranthene	205-99-2	3.80E-03	1.00E-02	NA	10	0.0019	0.005
Benzo[e]pyrene	192-97-2	2.00E-01	1.00E-02	NA	Not Listed	0.0058	0.005
Benzo[g,h,i]perylene	191-24-2	1.10E+02	1.00E-02	NA	10	0.0013	0.01
Benzo[k]fluoranthene	207-08-9	3.80E-03	1.00E-02	NA	10	0.0019	0.005
Chrysene	218-01-9	3.80E-03	1.00E-02	NA	10	0.0020	0.005
Dibenzo[a,h]anthracene	53-70-3	2.90E-03	1.00E-02	NA	10	0.0016	0.01
Dibenzothiophene ⁴	135-65-0	TBD	Not Listed	NA	Not Listed	0.0024	0.01
Fluoranthene	206-44-0	1.30E+02	1.00E-02	NA	10	0.0015	0.005
Fluorene	86-73-7	TBD	Not Listed	NA	10	0.0094	0.005
Indeno[1,2,3-c,d]-pyrene	193-39-5	3.80E-03	1.00E-02	NA	10	0.0017	0.01
Naphthalene	91-20-3	1.40E-01	5.00E-02	NA	10	0.0025	0.005
Perylene	198-55-0	1.10E+02	1.00E-02	NA	Not listed	0.0020	0.01
Phenanthrene	85-01-8	1.10E+03	2.00E-02	NA	10	0.0016	0.005
Pyrene	129-00-0	1.10E+02	1.00E-02	NA	10	0.0019	0.005
C1-Benzanthracene/chrysenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C1-Dibenzothiophenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C1-Fluorenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C1-Naphthalenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous

Analytical Group: PAH and Alkyl PAHs by Axys Laboratory SOP: MLA-021 R09

Concentration Level: Low (µg/L = microgram per liter)

Analyte	CAS Number	Project Action Limit ¹ (PAL)	Project Quantitation Limit Goal ² (PQLG)	Analytical Method ³		Achievable Laboratory Limits ³	
				MDLs	8270 QL	MDLs	QLs
C1-Phenanthrene/anthracenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C1-Pyrene/fluoranthenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C2-Benzanthracene/chrysenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C2-Dibenzothiophenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C2-Fluorenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C2-Naphthalenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C2-Phenanthrene/anthracenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C3-Benzanthracene/chrysenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C3-Dibenzothiophenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C3-Fluorenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C3-Naphthalenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C3-Phenanthrene/anthracenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C4-Benzanthracene/chrysenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C4-Dibenzothiophenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C4-Naphthalenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA
C4-Phenanthrenes/ anthracenes	NA	NA	1.00E-02	NA	Not Listed	NA	NA

Notes:

1. Project-specific action levels (PALs) are based on the CPGs listed PALs.
2. The PQLGs shown are those laboratory QLs taken from the CPG RI/FS QAPP, *Quality Assurance Project Plan/Field Sampling Plan Addendum Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection (July 2011)*. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data. Actual QLs will differ since the laboratory reports to sample specific detection limits.
3. Achievable MDLs listed are the statistically-derived MDLs. The QLs listed are based on CAS Laboratory's typical sample specific detection limits. Actual QLs may be higher and are dependent on the sample matrix effects. MDLs and QLs are limits that an individual laboratory can achieve when performing the analytical method.
4. This compound is not listed in SOC 8270P, therefore the related MDL and RL are estimated.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous

Analytical Group: Chlorinated Pesticides by EPA 1613 Modification

Concentration Level: Low (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ²	Analytical Method		Achievable Laboratory Limits	
				MDLs	Method CRQLs	MDLs	QLs
2,4'-DDD	53-19-0	3.10E-04	4.00E-04	Not Listed	Not Listed	5.0E-5	0.0002
2,4'-DDE	3424-82-6	2.20E-04	4.00E-04	Not Listed	Not Listed	2.0E-5	0.0002
2,4'-DDT	789-02-6	2.20E-04	4.00E-04	Not Listed	Not Listed	5.0E-5	0.0002
4,4,DDD	72-54-8	3.10E-04	4.00E-04	Not Listed	Not Listed	8.0E-5	0.0002
4,4,DDE	72-55-9	2.20E-04	4.00E-04	Not Listed	Not Listed	1.0E-5	0.0002
4,4,DDT	50-29-3	2.20E-04	4.00E-04	Not Listed	Not Listed	4.0E-5	0.0002
Aldrin	309-00-2	4.90E-05	4.00E-04	Not Listed	Not Listed	1.5E-4	0.0002
alpha-BHC	319-84-6	2.60E-03	4.00E-04	Not Listed	Not Listed	5.0E-5	0.0002
beta-BHC	319-85-7	9.10E-03	4.00E-04	Not Listed	Not Listed	6.0E-5	0.0002
cis-Chlordane (alpha Chlordane)	5103-71-9	1.00E-04	4.00E-04	Not Listed	Not Listed	6.0E-5	0.0002
cis-Nonachlor	5103-73-1	1.00E-04	4.00E-04	Not Listed	Not Listed	6.0E-5	0.0002
delta-BHC	319-86-8	2.60E-03	4.00E-04	Not Listed	Not Listed	4.0E-5	0.0005
Dieldrin	60-57-1	5.20E-05	4.00E-04	Not Listed	Not Listed	6.0E-5	0.0005
Endosulfan I	959-98-8	8.70E-03	4.00E-04	Not Listed	Not Listed	1.2E-4	0.0005
Endosulfan II	33213-65-9	8.70E-03	4.00E-04	Not Listed	Not Listed	1.6E-4	0.0005
Endosulfan sulfate	1031-07-8	8.70E-03	4.00E-04	Not Listed	Not Listed	1.6E-4	0.0005
Endrin	72-20-8	2.30E-03	4.00E-04	Not Listed	Not Listed	4.0E-5	0.0005
Endrin Aldehyde	7421-93-4	2.30E-03	4.00E-04	Not Listed	Not Listed	5.0E-5	0.0005
Endrin ketone	53494-70-5	2.30E-03	4.00E-04	Not Listed	Not Listed	5.0E-5	0.0005
gamma-BHC (Lindane)	58-89-9	1.60E-02	4.00E-04	Not Listed	Not Listed	5.0E-5	0.0002
Hexachlorobenzene	118-74-1	2.80E-04	4.00E-04	Not Listed	Not Listed	1.2E-4	0.0001
Heptachlor	76-44-8	7.90E-05	4.00E-04	Not Listed	Not Listed	7.0E-5	0.0002
Heptachlor Epoxide	1024-57-3	3.90E-05	4.00E-04	Not Listed	Not Listed	3.0E-5	0.0005
Methoxychlor	72-43-5	1.90E-02	4.00E-04	Not Listed	Not Listed	1.0E-5	0.001
Toxaphene	8001-35-2	TBD	Not on list of analytes	Not Listed	Not Listed	NA	NA
Oxychlordane	27304-13-8	1.00E-04	4.00E-04	Not Listed	Not Listed	1.4E-4	0.0002
Trans-Chlordane (gamma Chlordane)	5103-74-2	1.00E-04	4.00E-04	Not Listed	Not Listed	4.0E-5	0.0002
Trans-Nonachlor	3734-49-4	1.00E-04	4.00E-04	Not Listed	Not Listed	8.0E-5	0.0002

Notes:

1. Project-specific action levels are based on the CPGs listed action levels (PALs).

2. The PQLGs shown are those laboratory QLs taken from the CPG RI/FS *Quality Assurance Project Plan/Field Sampling Plan Addendum Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection (July 2011)*. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data. Actual QLs will differ since the laboratory reports to sample specific detection limits.
3. Achievable MDLs listed are the statistically-derived MDLs. The QLs listed are based on Axys Analytical Services typical sample specific detection limits. Actual QLs may be higher and are dependent on the sample matrix effects. MDLs and QLs are limits that an individual laboratory can achieve when performing the analytical method.
4. This analyte was not included on the PAH list in the CPG RI/FS QAPP.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ²	Analytical Method		Axys Achievable Laboratory Limits	
				MDLs (Estimated with interferences) ³	1668A Method QLs	MDLs	QLs ⁴
PCB-1	2051-60-7	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.90E-06	1.00E-06
PCB-2	2051-61-8	6.40E-05	4.00E-05	See Table 2 of method	1.00E-05	2.50E-06	1.00E-06
PCB-3	2051-62-9	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.80E-06	1.00E-06
PCB-4	13029-08-8	6.40E-05	6.00E-05	See Table 2 of method	5.00E-04	2.80E-06	2.0 E-06
PCB-5	16605-91-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-05	3.00E-06	2.0 E-06
PCB-6	25569-80-6	6.40E-05	4.00E-05	See Table 2 of method	5.00E-05	2.50E-06	2.0 E-06
PCB-7	33284-50-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-05	2.50E-06	2.0 E-06
PCB-8	34883-43-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.60E-06	2.0 E-06
PCB-9	34883-39-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-05	2.50E-06	2.0 E-06
PCB-10	33146-45-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-05	2.50E-06	2.0 E-06
PCB-11	2050-67-1	6.40E-05	6.00E-05	See Table 2 of method	2.00E-04	36.4E-06	2.0 E-06
PCB-12	2974-92-7	6.40E-05	6.00E-05, 6.00E-05, 4.00E-05	See Table 2 of method	1.00E-04	5.30E-06	2.0 E-06
PCB-13	2974-90-5					5.30E-06	2.0 E-06
PCB-14	34883-41-5					2.50E-06	2.0 E-06
PCB-15	2050-68-2	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.00E-06	2.0 E-06
PCB-16	38444-78-9	6.40E-05	4.00E-05	See Table 2 of method	1.00E-04	3.20E-06	1.0 E-06
PCB-17	37680-66-3	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.70E-06	1.0 E-06
PCB-18	37680-65-2	6.4E-05	6.00E-05	See Table 2 of method	5.00E-04	7.50E-06	1.0 E-06
PCB-19	38444-73-4	6.40E-05	4.00E-05	See Table 2 of method	1.00E-04	3.30E-06	1.0 E-06
PCB-20	38444-84-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.80E-06	1.0 E-06
PCB-21	55702-46-0	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	5.00E-06	1.0 E-06
PCB-22	38444-85-8	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.10E-06	1.00E-06
PCB-23	55720-44-0	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.20E-06	1.00E-06
PCB-24	55702-45-9	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	2.80E-06	1.00E-06
PCB-25	55712-37-3	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	2.50E-06	1.00E-06
PCB-26	38444-81-4	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	5.00E-06	1.00E-06
PCB-27	38444-76-7	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.50E-06	1.00E-06
PCB-28	7012-37-5	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.80E-06	1.00E-06

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ²	Analytical Method		Axys Achievable Laboratory Limits	
				MDLs (Estimated with interferences) ³	1668A Method QLs	MDLs	QLs ⁴
PCB-29	15862-07-4	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	5.00E-06	1.00E-06
PCB-30	35693-92-6	6.40E-05	6.00E-05	See Table 2 of method	5.00E-04	7.50E-06	1.00E-06
PCB-31	16606-02-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.50E-06	1.00E-06
PCB-32	38444-77-8	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	2.50E-06	1.00E-06
PCB-33	38444-86-9	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	5.00E-06	1.00E-06
PCB-34	37680-68-5	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	2.50E-06	1.00E-06
PCB-35	37680-69-6	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.60E-06	1.00E-06
PCB-36	38444-87-0	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	2.50E-06	1.00E-06
PCB-37	38444-90-5	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-38	53555-66-1	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	2.50E-06	1.00E-06
PCB-39	38444-88-1	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	2.50E-06	1.00E-06
PCB-40	38444-93-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	8.50E-06	1.00E-06
PCB-41	52663-59-9	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	8.50E-06	1.00E-06
PCB-42	36559-22-5	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	4.70E-06	1.00E-06
PCB-43	70362-46-8	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	5.00E-06	1.00E-06
PCB-44	41464-39-5	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.04E-05	1.00E-06
PCB-45	70362-45-7	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	5.00E-06	1.00E-06
PCB-46	41464-47-5	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	2.60E-06	1.00E-06
PCB-47	2437-79-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.04E-05	1.00E-06
PCB-48	70362-47-9	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.30E-06	1.00E-06
PCB-49	41464-40-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	8.10E-06	1.00E-06
PCB-50	62796-65-0	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	5.00E-06	1.00E-06
PCB-51	68194-04-7	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	5.00E-06	1.00E-06
PCB-52	35693-99-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.60E-06	1.00E-06
PCB-53	41464419	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	5.00E-06	1.00E-06
PCB-54	15968-05-5	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.10E-06	1.00E-06
PCB-55	74338-24-2	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ²	Analytical Method		Axys Achievable Laboratory Limits	
				MDLs (Estimated with interferences) ³	1668A Method QLs	MDLs	QLs ⁴
PCB-56	41464-43-1	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.10E-06	1.00E-06
PCB-57	70424-67-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-58	41464-49-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-59	74472-33-6	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	8.40E-06	1.00E-06
PCB-60	33025-41-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-61	33284-53-6	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.00E-05	1.00E-06
PCB-62	54230-22-7	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	8.40E-06	1.00E-06
PCB-63	74472-34-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.80E-06	1.00E-06
PCB-64	52663-58-8	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.50E-06	1.00E-06
PCB-65	33284-54-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.04E-05	1.00E-06
PCB-66	32598-10-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.90E-06	1.00E-06
PCB-67	73575-53-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.10E-06	1.00E-06
PCB-68	73575-52-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.00E-06	1.00E-06
PCB-69	60233-24-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	8.10E-06	1.00E-06
PCB-70	32598-11-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.00E-05	1.00E-06
PCB-71	41464-46-4	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	8.50E-06	1.00E-06
PCB-72	41464-42-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-73	74338-23-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.10E-06	1.00E-06
PCB-74	32690-93-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.00E-05	1.00E-06
PCB-75	32598-12-2	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	8.40E-06	1.00E-06
PCB-76	70362-48-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.00E-05	1.00E-06
PCB-77	32598-13-3	5.00E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-78	70362-49-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-79	41464-48-6	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-80	33284-52-5	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-81	70362-50-4	1.7E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-82	52663-62-4	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.30E-06	1.00E-06

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ²	Analytical Method		Axys Achievable Laboratory Limits	
				MDLs (Estimated with interferences) ³	1668A Method QLs	MDLs	QLs ⁴
PCB-83	60145-20-2	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.06E-05	1.00E-06
PCB-84	52663-60-2	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.80E-06	1.00E-06
PCB-85	65510-45-4	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	8.70E-06	1.00E-06
PCB-86	55312-69-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.28E-05	1.00E-06
PCB-87	38380-02-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.28E-05	1.00E-06
PCB-88	55215-17-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	6.60E-06	1.00E-06
PCB-89	73575-57-2	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.30E-06	1.00E-06
PCB-90	68194-07-0	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	1.96E-05	1.00E-06
PCB-91	68194-05-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	6.60E-06	1.00E-06
PCB-92	52663-61-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.60E-06	1.00E-06
PCB-93	73575-56-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.92E-05	1.00E-06
PCB-94	73575-55-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.70E-06	1.00E-06
PCB-95	38379-99-6	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.92E-05	1.00E-06
PCB-96	73575-54-9	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.60E-06	1.00E-06
PCB-97	41464-51-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.28E-05	1.00E-06
PCB-98	60233-25-2	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.92E-05	1.00E-06
PCB-99	38380-01-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.06E-05	1.00E-06
PCB-100	39485-83-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.92E-05	1.00E-06
PCB-101	37680-73-2	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	1.96E-05	1.00E-06
PCB-102	68194-06-9	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.92E-05	1.00E-06
PCB-103	60145-21-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.70E-06	1.00E-06
PCB-104	56558-16-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.20E-06	1.00E-06
PCB-105	32598-14-4	1.67E-04	4.00E-05	See Table 2 of method	2.00E-04	3.40E-06	1.00E-06
PCB-106	70424-69-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.10E-06	1.00E-06
PCB-107	70424-68-9	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	5.00E-06	1.00E-06
PCB-108	70362-41-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.28E-05	1.00E-06
PCB-109	74472-35-8	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	2.50E-06	1.00E-06

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ²	Analytical Method		Axys Achievable Laboratory Limits	
				MDLs (Estimated with interferences) ³	1668A Method QLs	MDLs	QLs ⁴
PCB-110	38380-03-9	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	1.32E-05	1.00E-06
PCB-111	39635-32-0	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	4.42E-06	1.00E-06
PCB-112	74472-36-9	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	5.10E-06	1.00E-06
PCB-113	68194-10-5	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	1.96E-05	1.00E-06
PCB-114	74472-37-0	1.67E-04	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-115	74472-38-1	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	1.32E-05	1.00E-06
PCB-116	18259-05-7	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	8.70E-06	1.00E-06
PCB-117	68194-11-6	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	8.70E-06	1.00E-06
PCB-118	31508-00-6	1.67E-05	4.00E-05	See Table 2 of method	5.00E-04	6.00E-06	1.00E-06
PCB-119	56558-17-9	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.28E-05	1.00E-06
PCB-120	68194-12-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.10E-06	1.00E-06
PCB-121	56558-18-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.70E-06	1.00E-06
PCB-122	76842-07-4	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-123	65510-44-3	1.67E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-124	70424-70-3	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-125	74472-39-2	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.28E-05	1.00E-06
PCB-126	57465-28-8	0.05E-06	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-127	39635-33-1	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-128	38380-07-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.00E-06	1.00E-06
PCB-129	55215-18-4	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.61E-05	1.00E-06
PCB-130	52663-66-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-131	61798-70-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.70E-06	1.00E-06
PCB-132	38380-05-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.50E-06	1.00E-06
PCB-133	35694-04-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.00E-06	1.00E-06
PCB-134	52704-70-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.00E-06	1.00E-06
PCB-135	52744-13-5	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.58E-05	1.00E-06
PCB-136	38411-22-2	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	3.30E-06	1.00E-06

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ²	Analytical Method		Axys Achievable Laboratory Limits	
				MDLs (Estimated with interferences) ³	1668A Method QLs	MDLs	QLs ⁴
PCB-137	35694-06-5	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.90E-06	1.00E-06
PCB-138	35065-28-2	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.61E-05	1.00E-06
PCB-139	56030-56-9	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.00E-06	1.00E-06
PCB-140	59291-64-4	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.00E-06	1.00E-06
PCB-141	52712-04-6	6.40E-05	4.00E-05	See Table 2 of method	2.00E-04	5.20E-06	1.00E-06
PCB-142	41411-61-4	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-143	68194-15-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.00E-06	1.00E-06
PCB-144	68194-14-9	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.60E-06	1.00E-06
PCB-145	74472-40-5	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.80E-06	1.00E-06
PCB-146	51908-16-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.80E-06	1.00E-06
PCB-147	68194-13-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.08E-05	1.00E-06
PCB-148	74472-41-6	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.20E-06	1.00E-06
PCB-149	38380-04-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.08E-05	1.00E-06
PCB-150	68194-08-1	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.20E-06	1.00E-06
PCB-151	52663-63-5	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.58E-05	1.00E-06
PCB-152	68194-09-2	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.50E-06	1.00E-06
PCB-153	35065-27-1	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.99E-05	1.00E-06
PCB-154	60145-22-4	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.58E-05	1.00E-06
PCB-155	33979-03-2	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.00E-06	1.00E-06
PCB-156	38380-08-4	1.67E-04	4.00E-05	See Table 2 of method	5.00E-04	5.00E-06	1.00E-06
PCB-157	69782-90-7	1.67E-04	4.00E-05	See Table 2 of method	5.00E-04	5.00E-06	1.00E-06
PCB-158	74472-42-7	6.40E-05	4.00E-05	See Table 2 of method	2.00E-05	2.50E-06	1.00E-06
PCB-159	39635-35-3	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-160	41411-62-5	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.61E-05	1.00E-06
PCB-161	74472-43-8	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-162	39635-34-2	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.90E-06	1.00E-06
PCB-163	74472-44-9	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.61E-05	1.00E-06

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ²	Analytical Method		Axys Achievable Laboratory Limits	
				MDLs (Estimated with interferences) ³	1668A Method QLs	MDLs	QLs ⁴
PCB-164	74472-45-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	3.40E-06	1.00E-06
PCB-165	74472-46-1	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-166	41411-63-6	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.00E-06	1.00E-06
PCB-167	52663-72-6	1.67E-04	4.00E-05	See Table 2 of method	5.00E-04	2.70E-06	1.00E-06
PCB-168	59291-65-5	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.99E-05	1.00E-06
PCB-169	32774-16-6	1.67E-05	4.00E-05	See Table 2 of method	5.00E-04	2.90E-06	1.00E-06
PCB-170	35065-30-6	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.70E-06	1.00E-06
PCB-171	52663-71-5	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	6.30E-06	1.00E-06
PCB-172	52663-74-8	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.80E-06	1.00E-06
PCB-173	68194-16-1	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	6.30E-06	1.00E-06
PCB-174	38411-25-5	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.70E-06	1.00E-06
PCB-175	40186-70-7	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	4.10E-06	1.00E-06
PCB-176	52663-65-7	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.60E-06	1.00E-06
PCB-177	52663-70-4	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.70E-06	1.00E-06
PCB-178	52663-67-9	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.00E-06	1.00E-06
PCB-179	52663-64-6	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	4.80E-06	1.00E-06
PCB-180	35065-29-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.27E-05	1.00E-06
PCB-181	74472-47-2	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	4.30E-06	1.00E-06
PCB-182	60145-23-5	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	4.50E-06	1.00E-06
PCB-183	52663-69-1	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	8.40E-06	1.00E-06
PCB-184	74472-48-3	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.80E-06	1.00E-06
PCB-185	52712-05-7	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	8.40E-06	1.00E-06
PCB-186	74472-49-4	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	5.30E-06	1.00E-06
PCB-187	52663-68-0	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.17E-05	1.00E-06
PCB-188	74487-85-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-190	41411-64-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-191	74472-50-7	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.40E-06	1.00E-06

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous
Analytical Group: PCB Congeners by EPA 1668A (MLA-010)
Concentration Level: (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ²	Analytical Method		Axys Achievable Laboratory Limits	
				MDLs (Estimated with interferences) ³	1668A Method QLs	MDLs	QLs ⁴
PCB-192	74472-51-8	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-193	69782-91-8	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	1.27E-05	1.00E-06
PCB-194	35694-08-7	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.50E-06	1.00E-06
PCB-195	52663-78-2	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.70E-06	1.00E-06
PCB-196	42740-50-1	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	4.00E-06	1.00E-06
PCB-197	33091-17-7	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	7.70E-06	1.00E-06
PCB-198	68194-17-2	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.10E-06	1.00E-06
PCB-199	52663-75-9	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	5.10E-06	1.00E-06
PCB-200	52663-73-7	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	7.70E-06	1.00E-06
PCB-201	40186-71-8	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.80E-06	1.00E-06
PCB-202	2136-99-4	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.50E-06	1.00E-06
PCB-203	52663-76-0	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-204	74472-52-9	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.10E-06	1.00E-06
PCB-205	74472-53-0	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-206	40186-72-9	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-207	52663-79-3	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	2.50E-06	1.00E-06
PCB-208	52663-77-1	6.40E-05	4.00E-05	See Table 2 of method	1.00E-03	3.30E-06	1.00E-06
PCB-209	2051-24-3	6.40E-05	4.00E-05	See Table 2 of method	5.00E-04	2.60E-06	1.00E-06

Notes:

1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The project quantitation limit goals (PQLGs) are the Achievable Laboratory QLs for individual PCB Congeners listed in the CPG RI/FS QAPP, *Quality Assurance Project Plan/Field Sampling Plan Addendum Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection (July 2011)*. Values range from 4.00E-05 to 6.00E-05
3. See Method 1688A Table 2 for a list of PCB Congener MDLs.
4. Achievable QLs shown are based on typical Axys Analytical Services detection limits expected to range from 0.1 to 2.0 µg/L, with some exceptions, in particular for the co-eluting PCB congeners. The laboratory will report the PCB congeners to sample specific detection limits, which will be different from that shown in this worksheet but need to be low enough to support split sample comparison. Actual QLs may be higher dependent on sample matrix effects.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous

Analytical Group: PCDD/PCDF by EPA 1613B

Concentration Level: Low (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goals ²	EPA 1613B Analytical Method ³		Method 1613B Achievable Laboratory Limits	
				MDLs (µg/L) ³	Method CRQLs ³	MDLs (µg/L) ⁴	QLs (µg/L) ⁴
2378-TCDD	1746-01-6	5.00E-09	5	NA	1.0E-05	4.4E-07	0.5E-06
12378-PeCDD	40321-76-4	5.00E-09	25	NA	5.0E-05	1.6E-06	0.5E-06
123678-HxCDD	57653-85-7	5.00E-08	25	NA	5.0E-05	1.8E-06	0.5E-06
123478-HxCDD	39227-28-6	5.00E-08	25	NA	5.0E-05	1.3E-06	0.5E-06
123789-HxCDD	19408-74-3	5.00E-08	25	NA	5.0E-05	1.2E-06	0.5E-06
1234678-HpCDD	35822-46-9	5.00E-07	25	NA	5.0E-05	1.4E-06	0.5E-06
OCDD	3268-87-9	1.70E-05	50	NA	1.0E-06	4.1E-06	0.5E-06
2378-TCDF	51207-31-9	5.00E-08	5	NA	1.0E-05	4.5E-07	0.5E-06
12378-PeCDF	57117-41-6	1.70E-07	25	NA	5.0E-05	2.0E-06	0.5E-06
23478-PeCDF	57117-31-4	1.70E-08	25	NA	5.0E-05	1.8E-06	0.5E-06
123678-HxCDF	57117-44-9	5.00E-08	25	NA	5.0E-05	8.2E-07	0.5E-06
123789-HxCDF	72918-21-9	5.00E-08	25	NA	5.0E-05	2.2E-06	0.5E-06
123478-HxCDF	70648-26-9	5.00E-08	25	NA	5.0E-05	9.2E-07	0.5E-06
234678-HxCDF	60851-34-5	5.00E-08	25	NA	5.0E-05	1.4E-06	0.5E-06
1234678-HpCDF	67562-39-4	5.00E-07	25	NA	5.0E-05	1.2E-06	0.5E-06
1234789-HpCDF	55673-89-7	5.00E-07	25	NA	5.0E-05	9.7E-07	0.5E-06
OCDF	39001-02-0	1.70E-05	50	NA	1.0E-06	2.8E-06	0.5E-06

Notes:

1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The project quantitation limit goals (PQLGs) are the Achievable Laboratory QLs for individual PCDDs/PCDFs based on the CPG goals which are derived from the lower of *Quality Assurance Project Plan/Field Sampling Plan Addendum Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection (July 2011)*. The split sample data limit should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
3. Specific MDLs are not given in USEPA Method 1613B, but the QLs listed are the minimum levels published in Table 2 of USEPA Method 1613B. The actual detection limits are usually dependent on the level of interference rather than instrument limitations.
4. The MDLs listed are the statistically-derived MDLs. The QLs listed are obtained from Axys Analytical Services. Actual QLs may be higher and are dependent on the sample matrix effects.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous

Analytical Group: Metals by SW-846, 6020

Concentration Level: Low (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ²	6020 Analytical Method ³		Achievable Laboratory Limits ^{3,4}	
				MDLs ³	CRQLs	MDLs	QLs
Aluminum	7429-90-5	5.00E+01	2.0	Not Listed	Not Listed	1.8	40
Antimony	7440-36-0	1.5	0.05	Not Listed	Not Listed	0.097	1.0
Arsenic	7440-38-2	1.70E-02	0.5	Not Listed	Not Listed	0.26	1.0
Barium	7440-39-3	4.00E+00	0.05	Not Listed	Not Listed	0.045	5.0
Beryllium	7440-41-7	6.60E-01	0.02	Not Listed	Not Listed	0.028	0.40
Cadmium	7440-43-9	1.80E-01	0.02	Not Listed	Not Listed	0.059	0.10
Calcium	7440-70-2	NA	4.0	Not Listed	Not Listed	13	200
Chromium	7440-47-3	4.30E-02	0.2	Not Listed	Not Listed	0.35	5.0
Cobalt	7440-48-4	1.10E+00	0.02	Not Listed	Not Listed	0.029	5.0
Copper	7440-50-8	3.10E+00	0.1	Not Listed	Not Listed	0.15	1.0
Iron	7439-89-6	3.00E+02	10	Not Listed	Not Listed	5.7	20
Lead ⁴	7439-92-1	2.50E+00	0.02	Not Listed	Not Listed	0.047	1.0
Magnesium	7439-95-4	NA	2	Not Listed	Not Listed	0.94	50
Manganese	7439-96-5	5.00E+01	0.05	Not Listed	Not Listed	0.20	5.0
Nickel	7440-02-0	8.20E+00	0.2	Not Listed	Not Listed	0.28	5.0
Potassium	7440-09-7	NA	100	Not Listed	Not Listed	6.0	200
Selenium	7782-49-2	5.00E+00	1.0	Not Listed	Not Listed	0.25	1.0
Silver	7440-22-4	3.60E-01	0.02	Not Listed	Not Listed	0.011	1.0
Sodium	7440-23-5	NA	200	Not Listed	Not Listed	4.0	200
Thallium	7440-28-0	3.70E-02	0.02	Not Listed	Not Listed	0.076	0.50
Titanium	7440-32-6	1.50E-04	1.0	Not Listed	Not Listed	0.54	5.0
Vanadium	7440-62-2	1.80E+01	0.2	Not Listed	Not Listed	1.5	5.0
Zinc	7440-66-6	8.10E+01	0.5	Not Listed	Not Listed	1.5	10

Notes:

1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The PQLGs shown are those laboratory QLs taken from the CPG RI/FS *Quality Assurance Project Plan/Field Sampling Plan Addendum Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection (July 2011)*. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered in data comparison.
3. The achievable QLs are for Shealy Laboratories by ICP-MS. The actual reported limits will differ and are dependent on the sample matrix effects.
4. Many laboratory QLs are above the CPG target QLs, but the laboratory will report the metals data to the MDLs. Differences in laboratory method sensitivity must be considered when evaluating the split sample results.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous

Analytical Group: Mercury by EPA 1630

Concentration Level: Trace (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goals ²	Analytical Method ³		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs ⁴
Mercury	7439-97-6	5.00E-02	1.00E-03	2.0E-04	5.0E-04	2.0E-04	5.0E-04

Notes:

1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The PQLGs shown are those laboratory QLs taken from the CPG RI/FS *Quality Assurance Project Plan/Field Sampling Plan Addendum Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection (July 2011)*. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
3. Method MDLs are suggested values.
4. Actual QLs may be higher and are dependent on the sample matrix effects.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous

Analytical Group: Methyl mercury by EPA 1631

Concentration Level: Trace (µg/L)

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goals ²	EPA 1630 Analytical Method		Achievable Laboratory Limits	
				MDLs	Method QLs	MDLs	QLs ^{4, 3}
Methyl mercury	22967-92-6	2.80E-03	5.00E-05	2.0E-05	6.0E-05	1.7E-05 ng/L	5.0E-05 ng/L

Notes:

1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The PQLGs listed are the achievable laboratory QLs listed in the CPG's *Quality Assurance Project Plan/Field Sampling Plan Addendum Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection (July 2010)*. The split sample data should be low enough for data comparison. Differences in laboratory detection limits will be considered when comparing the data.
3. The achievable QLs listed will differ dependent on the laboratory assigned to perform the analyses.
4. Actual QLs may be higher and are dependent on the sample matrix effects.

QAPP Worksheet #15
Reference Limits and Evaluation Table

Matrix: Aqueous

Analytical Group: Chemical Water Column Analyses

Concentration Level: Low

Analyte	CAS Number	Project Action Limit ¹	Project Quantitation Limit Goal ² (mg/L)	Analytical Method		Achievable DESA Laboratory Limits ³	
				MDLs (µg/L)	Method QLs (µg/L)	MDLs (mg/ L)	QLs (mg/L)
Dissolved Hexavalent Chromium ⁵	18540299	0.043 (µg/L)	10 (µg/L)	TBD (Per EPA Method 218.6, MDL = 0.2-0.3 µg/L and IMDL = 1.4 µg/L)		6.21 µg/L	10 µg/L (DESA limits are from DESA SOP C-96 which is based on Standard Method (SM) 3500-CrB and method HACH 8023) Final method TBD
TDS	NA	1.00E+03 (µg/L)	5.00E+03 µg/L	NA	Not listed in Method SM2540D	NA	TBD
TOC	10-19-5	NA	300 µg/L	NA	SOP - C-83	0.19 µg/L	1.0 µg/L
DOC	NA	None	0.3	NA	Not listed in Method SM5310B	0.25	0.5
POC	NA	None	1.3	NA	Not listed in EPA Method 415.1	0.005	0.01
SSC (1.5 µm filter)	NA	None	1.0 (no goal listed in CPG's QAPP)	NA	Not listed in Method SM 2540D ⁴	NA	1.0 (with > 1L volume sample)

Notes: Laboratory results will be reported in dry weight.

1. Project-specific action levels are based on the CPGs listed action levels (PALs).
2. The target PQLG listed is based on the CPG's laboratory achievable QL. Differences in laboratory detection limits will be considered when comparing the data.
3. Laboratory QL is anticipated to be low enough to allow comparison of the split sample data to the CPG data. Detection limits are based on communications with Jim Ferretti of the DESA laboratory and are derived from a DESA study conducted on water column samples from the New York Bight study. The MDL for POC and DOC are estimates and are one half of the QL.
4. Method SM 2540D is equivalent to ASTM 3977-97 Test Option B.
5. CPG is using EPA method 218.6

QAPP Worksheet #16
Project Schedule Timeline Table

Activities	Organization	Anticipated Date(s) of Initiation	Anticipated Date of Completion	Deliverable	Deliverable Due Date
Prepare and submit: Oversight QAPP Addendum for Chemical Water Column Study to EPA and USACE	CDM	May 9, 2011	May 23, 2011	UFP-QAPP addendum, Draft	May 23, 2011
Prepare and submit: Final oversight QAPP Addendum for Chemical Water Column Study	CDM	As soon as comments are received	August 2, 2011	UFP-QAPP addendum, Final	August 2, 2011
Acceptance of splits and sample handling activities	CDM	Summer 2011 – Summer 2012	10 days after commencement date	Summary report of chemical data	To be determined
Laboratory Analysis	CDM subcontract laboratory(ies)	Summer 2011 – Summer 2012	Summer 2012 (Exact date to be determined; data collection will be dependent on the CPG schedule)	Data Package	To be determined; will be dependent on the CPG schedule For standard analyses, 21 days after the last sample is received; however, specialized analyses may take additional time
Validation and verification of sample data	CDM	Summer 2011 – Summer 2012	Fall 2012	Validated data report	To be determined; will be dependent on CPG schedule
Oversight /Data Evaluation	CDM	To be determined	To be determined	Oversight data Comparison and Summary Report/ Data Quality Summary Report	To be determined
Review Chemical Water Column Study Analysis Data Report	CDM	90 days after each sampling event	1 month after receipt of report	Comments on Chemical Water Column Study Analysis Data Report	1 month after receipt of report

QAPP Worksheet #18
Sampling Locations and Methods/SOP Requirements Table

Survey Location ID	Media	Analytical Group	Concentration Level	Estimated Number of Samples (identify field duplicates)	Sampling SOP Reference	Rationale for Sampling Location
Refer to QAPP prepared by AECOM for the CPG and Figure 1 (Lower Passaic Locations only)	Aqueous samples	Analytical group A for split samples includes: PCB congeners, PCDD/PCDF congeners, metals (total and dissolved), DOC, POC, SSC, and TOC	Low	Approximately 10 percent of CPG samples will be split.	Appendix B of CPG’s CWCM QAPP (AECOM 2011) (also see footnotes)	Split samples will be accepted judgmentally by the on-site oversight staff in consultation with the PM and USACE/EPA
		Analytical group B for split samples includes: PAHs, alkyl PAHs, Chlorinated pesticides, TAL metals, a subset of TAL metals in dissolved phase (arsenic, cadmium, chromium, copper, lead, nickel, selenium, and zinc), titanium, methyl mercury (total and dissolved), and hexavalent chromium (dissolved only)	Low	Approximately 10 percent of CPG samples will be split plus a PE sample for organics and metals will be submitted in alternate sampling events.		
See Worksheet #20 for number of split samples. See CPG’s QAPP Worksheet No.18 for the sampling locations and sampling rationale.						

Notes:

Refer to the QAPP prepared by AECOM for the CPG (Worksheets #10, 11 and 18 and Figure 1) titled, *Quality Assurance Project Plan/Field Sampling Plan Addendum Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection (July 2011)* for sampling information. Samples will be split by simultaneous filling of the sample bottles using an in-line splitter and associated tubing. CDM and Louis Berger will submit PE samples in alternate sampling events.

Lower Passaic locations vary depending on the Event type as described in the CPG's QAPP and FSP Addendum. They include Dundee Dam, Saddle River, Second River, Third River, river mile (RM) 10.2 or RM 13.5, RM 6.7, RM 4.2, RM 1.4 and RM 0. The location of Tidal 1 (applicable when flows are < 1,000 cfs) is based on the location of the salt wedge located approximately one mile downstream of the predicted location of the salt wedge; Tidal 2 (applicable when flows are < 1,000 cfs) is based on the location of the salt wedge and the location of Tidal 1. Tidal 2 will be located halfway between Tidal 1 and RM 1.4, but not upstream of RM 4.2.

**QAPP Worksheet #19 – Surface Water Analysis
 Analytical SOP Requirements Table**

Matrix ¹	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference ²	Sample Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light) ³	Maximum Holding Time (preparation/analysis)
AXYS Laboratory							
Aqueous	PAH and Alkyl PAHs (Group B)	Low	Modified SW-846 Method 8270C (Axsy SOP MLA-021)	1L	1L amber glass	Fill bottle to top (no headspace); 4±2°C; store in dark	Extract within 7 days and analyze within 40 days of extraction
Aqueous	Chlorinated pesticides	Low	USEPA 1613 modified Axsy SOP MLA-035	2L	2 × 1L amber glass	Fill bottle to top (no headspace); 4±2°C; store in dark	Extract within 7 days and analyze within 40 days of extraction
Aqueous	PCB Congeners (Group A)	Low	USEPA 1668A (Axsy SOP MLA-010)	1L	1L amber glass	Fill bottle to top (no headspace); 4±2°C; store in the dark	1 year for preparation and analysis
Aqueous	PCDD/PCDF (Group A)	Low	EPA 1613B (Axsy SOP MLA-017)	1L	1L amber glass	Fill bottle to top (no headspace); 4±2°C; store in the dark	1 year for preparation and analysis
Shealy							
Aqueous	Total and Dissolved Metals (Cadmium, copper and lead) (Group A)	Low	SW-846 Method 6020 (Shealy SOP S-IM-021) (Inductively Coupled Plasma – Mass Spectrometry (ICP-MS))	1L each	2 × 1L HDPE (total and filtered) [1 bottle needed for total or dissolved when both groups A and B are being sampled]	Fill bottle to top (no headspace); 4±2°C; Preserve with nitric acid (HNO ₃)	Preservation within 48 hours; 6 months for preparation and analysis
Aqueous	Total TAL Metals and Titanium) (Group B)	Low	SW-846 Method 6020 (Shealy SOP S-IM-021) (ICP-MS)	1L	1L HDPE [1 bottle needed when groups A and B total metals are being sampled]	Fill bottle to top (no headspace); 4±2°C; Preserve with nitric acid (HNO ₃)	Preservation within 48 hours; 6 months for preparation and analysis

**QAPP Worksheet #19 – Surface Water Analysis
Analytical SOP Requirements Table**

Matrix ¹	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference ²	Sample Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light) ³	Maximum Holding Time (preparation/analysis)
Aqueous	Dissolved Metals (Arsenic, cadmium, chromium, copper, lead, nickel, selenium, and zinc)(Group B)	Low	SW-846 Method 6020 (Shealy SOP S-IM-021) (ICP-MS)	1L	1L HDPE (filtered) [1 bottle needed when both groups A and B are being sampled]	Fill bottle to top (no headspace); 4±2°C; Preserve with nitric acid (HNO ₃)	Preservation within 48 hours; 6 months for preparation and analysis
Microbac Laboratory							
Aqueous	Mercury (Hg) total and dissolved (Group A)	Low	Microbac SOP Hg-1631 Rev. 0	500 mL	2x250 mL glass bottle	Fill bottle to top (no headspace); 4±2°C; Preserve with HNO ₃	Preservation within 28 days; 90 days from collection to analysis
Aqueous	Methyl mercury (Group B)	Low	Microbac SOP Hg-1630 Rev. 0	250 mL total and 250 mL dissolved	2 × 250 mL fluoropolymer bottle	Fill bottle to top (no headspace); 4±2°C; Preserve with hydrochloric acid (HCL)	Preservation within 48 hours; 6 months for preparation and analysis
DESA							
Aqueous	Hexavalent Chromium (Group B)	Low	SM3500 (DESA SOP C-96)	125 mL	250mL HDPE	Cool to 4±2°C	Lab preserved; 24 hours for preparation and analysis
Aqueous	TDS	Low	SM2540D (DESA SOP C-37 Modified)	250 mL	(1) 250 mL amber glass bottle or protect from light	Cool to 4°C; No headspace	Ship to the laboratory and preserve within 48 hours. 7 days to analysis
Aqueous	TOC (Group A)	Low	SM5310B (DESA SOP C-83)	120 mL	(1) 250 mL amber glass bottle or protect from light	H ₂ SO ₄ to pH <2; Cool to 4°C	Ship to the laboratory and preserve within 48 hours. 28 days to analysis
Aqueous	DOC (Group A)	Low	DOC: SM5310B (DESA SOP C-88 Modified)	600 mL	(3) 200 mL amber glass bottle or protect from light	Filter, H ₂ SO ₄ to pH <2; Cool to 4°C; No headspace	Ship to the laboratory and filtered within 48 hours. Filters and filtrates must be analyzed within 28 days.
Aqueous	POC (Group A)	Low	POC: USEPA 415.1 (DESA SOP C-83 Modified)				

QAPP Worksheet #19 – Surface Water Analysis
Analytical SOP Requirements Table

Matrix ¹	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference ²	Sample Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light) ³	Maximum Holding Time (preparation/analysis)
Aqueous	SSC	Low	SM2540D (DESA SOP C-33 Modified)	1000 mL	(1) 1 L HDPE	Cool to 4°C	28 days to analysis

Notes:

1. Preservative to be added at laboratory if unable to take pre-preserved bottles on boat during sampling. CDM will determine with the labs which samples will be preserved at the laboratories.
2. The CDM analytical subcontract laboratory SOPs for these analyses are shown in Appendix M of this QAPP. Method modifications are outlined in the laboratory SOP in Appendix M. The Axyx laboratory SOPs are proprietary but SOP summaries are included herein.
3. The actual jar size may vary depending on the need of the assigned laboratory. The sampler should confirm sample volumes with the laboratory prior to mobilizing to the field. Samples may be shipped to the laboratories unpreserved for preservation by the laboratory.

QAPP Worksheet #20
Field Quality Control Sample Summary Table

Matrix	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference	No. of Split Sampling Locations	No. of Field Duplicate Pairs	No. of Extra Volume Laboratory QC (e.g., MS/MSD or Duplicate) Samples	No. of Equipment Rinsate Blanks ³	No. of Trip. Blanks	No of PE ⁴ Samples	Total No. of Samples
Analyte Group A²										
Aqueous	PCB congeners	Low	USEPA 1668A (AxyS SOP MLA-010)	38	1 per sampling event (8)	NA	(Ambient blank) 2	0	1 per alternate event (4)	52
Aqueous	PCDD/PCDF	Low	EPA 1613B (AxyS SOP MLA-017)	38	8	1 per 20, per SDG or 1 per sampling event	2	0	4	52
Aqueous	TDS	Low	SM2540D (DESA SOP C-37 Modified)	38	8	1 per 20 or 1 per sampling event	0	0	0	46
Aqueous	TOC	Low	SM5310B (DESA SOP C-83)	38	8	1 per 20 or 1 per sampling event	0	0	0	46
Aqueous	DOC	Low	DOC: SM5310B (DESA SOP C-88 Modified)	38	8	0 MS; 1 duplicate per 20 or per sampling event	0	0	0	46
Aqueous	POC	Low	POC: USEPA 415.1 (DESA SOP C-83 Modified)	38	8	0 MS; 1 duplicate per 20 or per sampling event	0	0	0	46
Aqueous	SSC	Low	SM2540D (DESA SOP C-33 Modified)	38	8	0 MS; 1 duplicate per 20 or per sampling event	0	0	0	46
Split samples will be collected for Group A analyses as follows: 22 from Routine events, 12 from High flow events and 4 from the Low flow events plus the QC samples numerated above.										
Analyte Group B²										
Aqueous	PAHs	Low	Modified SW-846 Method 8270C (AxyS SOP MLA-021)	24	8	1 per 20, per SDG or 1 per sampling event	2	0	4	38
Aqueous	Alkyl PAHs	Low	Modified SW-846 Method 8270C (AxyS SOP MLA-021)	24	8	1 per 20, per SDG or 1 per sampling event	2	0	4	36

QAPP Worksheet #20
Field Quality Control Sample Summary Table

Matrix	Analytical Group	Concentration Level	Analytical and Preparation SOP Reference	No. of Split Sampling Locations	No. of Field Duplicate Pairs	No. of Extra Volume Laboratory QC (e.g., MS/MSD or Duplicate) Samples	No. of Equipment Rinsate Blanks ³	No. of Trip. Blanks	No of PE ⁴ Samples	Total No. of Samples
Aqueous	Chlorinated Pesticides	Low	Axys SOP MLA-035	24	8	per 20, per SDG or 1 per sampling event	2	0	4	36
Aqueous	Total and Dissolved Metals (Dissolved metals- arsenic, cadmium, copper, chromium, lead, nickel, selenium, and zinc)	Low	Shealy SOP S-IM-021 for SW-846 Method 6020	24	8	1 per 20, per SDG or 1 per sampling event	2	0	1 per event (4)	36
Aqueous	Total and Dissolved Mercury	Low	Microbac SOP for EPA Method 1630	24	8	per 20, per SDG or 1 per sampling event	2	0	4	36
Aqueous	Total and Dissolved Methylmercury	Low	Microbac SOP for EPA Method 1631	24	8	per 20, per SDG or 1 per sampling event	2	0	4	36
Aqueous	Dissolved Hexavalent Chromium	Low	SM3500 (DESA SOP C-96)	24	8	per 20, per SDG or 1 per sampling event	2	0	4	36
Split samples will be collected for Group B analyses as follows: 13 from Routine events, 6 from High flow events and 4 from the Low flow events plus the QC samples numerated above..										

Notes:

1. The Field and Analytical Services Teaming Advisory Committee (FASTAC) decision process is required for obtaining laboratory services. However for this project it is critical for CDM and Louis Berger to mirror the CPG's analytical procedures in addition to maintaining similar volumes to provide comparable data and detection limits. This limits the number of laboratories and the methods which can be used. Low concentrations and flexibility are required for the Passaic project. Also due to the difficulty of analyzing the sample matrix for the selected analyses subcontract laboratories are being used to supplement DESA services to ensure accurate results, to reduce uncertainties in the measurements and to obtain data comparable with data from previous and future surveys and with the CPG's data. PAH, alkyl PAH, chlorinated pesticides, PCB congeners, and dioxin/furans will be analyzed by Axys laboratory. CDM subcontracted one of its master services agreement laboratories, Shealy, to obtain analytical services for the TAL metals analyses, and mercury and methylmercury which will both be analyzed by Microbac laboratory. DESA will be requested to perform the remaining wet chemistry parameters and hexavalent chromium.
2. Refer to Worksheet #11 for the field sampling event in which sample parameters will be split.
3. Rinsate blanks will be prepared near the beginning and near the end of all the CWCM sampling events.
4. PE samples will be documented on the chain of custody form. PE samples will be submitted by CDM (4) and Louis Berger (4) for analysis in alternate sampling events over the course of eight events.

QAPP Worksheet #23
Analytical SOP References Table

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work?
USEPA Methods 8270C/D Alys SOP: MLA-021	<i>Analytical Method for the Determination of Polycyclic Aromatic Hydrocarbons (PAH), and Alkylated PAHs and Alkanes, Laboratory SOP MLA-021, Revision 10.02, March 2011.</i>	Definitive	PAH and Alkyl PAH	Low-resolution mass spectrometry (LRMS)	Alys Analytical Services Laboratory 2045 Mills Road West Sidney, British Columbia, Canada Contact: Candice Navaroli Phone:1-888-373-0881	No
EPA 1613B Modified/ Alys SOP: MLA-035, R06	<i>Analytical Method for the Analysis of the Analysis of Multi-Residue Pesticides by HRGC/HRMS, Laboratory SOP MLA-035, Revision 6, July 2010 [Summary MSU-035]</i>	Definitive	Chlorinated Pesticides	High-resolution gas chromatograph / high-resolution mass spectrometry (HRGC/HRMS)	Alys Analytical Services	Analyte list per WS#15
EPA 1668 for HRGC/HRMS Alys SOP: MLA-10	<i>Analytical Method for the Determination of: 209 PCB Congeners Laboratory SOP MLA-010, Revision 10, August 2010.</i>	Definitive	PCB Congeners	HRGC/HRMS	Alys Analytical Services	No
EPA 1613B for HRGC/HRMS Alys SOP: MLA-017	<i>Analytical Method for the Determination of Polychlorinated Dibenzodioxins and Dibenzofurans Laboratory SOP MLA-017, Revision 20, March 2011.</i>	Definitive	PCDD/PCDF	HRGC/HRMS	Alys Analytical Services	No
EPA 6020 Shealy SOP: S-IM-021, Rev 2	<i>Standard Operating Procedure: Inductively Coupled Plasma – Mass Spectrometry Analysis Method 6020A, Laboratory SOP S-IM-021, Revision 2, April 1, 2011</i>	Definitive	Metals	ICP-MS	Shealy Environmental, Inc. 106 Vantage Point Drive West Columbia, SC 29172 Attention: Nisreen Saikaly 1-800-673-9375	No
EPA 1631 Microbac SOP: Hg-1631, Rev. 2	<i>Total Mercury Using Atomic Fluorescence Spectroscopy. Rev. 2. August 28, 2009</i>	Definitive	Mercury (total and dissolved)	Cold vapor atomic fluorescence spectrometry (CVAFS)	Microbac Laboratories, Inc. 250 West 84 th Drive Merrillville, IN 46410 Attention: Kevin Falvey 219-769-8378	No
EPA 1630 Microbac SOP: Methyl Mercury Draft, Rev. 0	<i>Draft Methylmercury Using Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence. July 27, 2010.</i>	Definitive	Methyl mercury (total and dissolved)	CVAFS	Microbac Laboratories, Merrillville, Indiana	No
DESA SOP C-96	<i>Standard Operating Procedure: Hexavalent Chromium. DESA SOP C-96, Revision 2.1, January 31, 2009.</i>	Definitive	Hexavalent Chromium (dissolved)	Colorimeter	USEPA Region 2 – DESA 2890 Woodbridge Avenue Edison, NJ 08937 Contact: John Birri	No

QAPP Worksheet #23
Analytical SOP References Table

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work?
TDS (SM2540C)	Modified: "Standard Operating Procedure: Total Dissolved Solids." DESA SOP C-37, Revision 2.1, January 2009.	Definitive	TDS (laboratory filtered)	Gravimetric	DESA	Y (0.7 µm filter will be used for TDS)
SM 5310B - DESA SOP C-83 Modified	Modified: "Standard Operating Procedure: Total Organic Carbon." DESA SOP C-83, Revision 2.1, January 31, 2009.	Definitive	TOC (Total Organic Carbon)	Organic Carbon Analyzer	DESA	Yes – see below
Project-specific Modification: Use combustible 0.7 µm glass fiber filter (Whatman, 25 mm diameter, Model 1825-025). Filter within 48 hours of sample collection and preserve. Expose to HCl fumes to remove inorganic carbon. Combust entire filter to reduce errors. Reported DOC values will be the average of two analyses.						
SM 5310B - DESA SOP C-83 Modified	Modified: "Standard Operating Procedure: Total Organic Carbon." DESA SOP C-83, Revision 2.1, January 31, 2009.	Definitive	DOC (Dissolved Organic Carbon)	Organic Carbon Analyzer	DESA	Yes – see below
Project-specific Modification: Use combustible 0.7 µm glass fiber filter (Whatman, 25 mm diameter, Model 1825-025). Filter within 48 hours of sample collection and preserve. Expose to HCl fumes to remove inorganic carbon. Combust entire filter to reduce errors. Reported DOC values will be the average of two analyses.						
EPA 415.1- DESA SOP C-88 Modified	Modified: "Standard Operating Procedure: Total Organic Carbon -Sediment." DESA SOP C-88, Revision 2.1, January 31, 2009.	Definitive	POC (Particulate Organic Carbon)	Filter and Carbon Analyzer with IR or flame ionization detector (FID) Detector	DESA	Yes – see below
Project-specific Modification: Use a 0.7 µm glass fiber filter (Whatman, 25 mm diameter, Model 1825-025). Filters will be pre-combusted and tared; after filtration, filters will be dried and re-weighed. The mass of suspended solids on the 0.7 µm filter will be reported in the data package. Dried POC filters will be stored frozen until analysis. Prior to combustion, POC filter will be exposed to hydrochloric fumes for 24 hours to remove inorganic carbon. DESA will communicate with CDM if the suspended solids concentration is relatively high and carbon load may saturate the detector. POC will be reported in units of mg/L (i.e., volume of water filtered).						
SM 2540D - DESA SOP C-33 Modified	Modified: "Standard Operating Procedure: Total Suspended Solids Volatile Suspended Solids." DESA SOP C-33, Revision 3.1, January 31, 2009.	Definitive	Suspended Solids (total suspend solids = TSS)	Filter, Oven, balance	FASTAC implementation DESA	Yes – see below
Project-specific Modification: Use 0.7 µm filter (ProWeigh, Environmental Express, Model F93447MM-X). Use entire sample bottle to filter. Rinse with deionized water to capture all the solids or until filter refusal. Filter within 7 days of collection. DESA will communicate with CDM if the suspended solids concentration is relatively high and may clog the filter.						

Notes:

1. The FASTAC policy for procuring analytical services was implemented; DESA will perform analyses. DESA maintains the laboratory's SOP information. The SOP will be modified to facilitate comparison with the CPG data. A trip report is not required for samples shipped to the DESA laboratory.
2. As necessary, the assigned laboratories will perform additional clean-up of split samples (via gel permeation chromatography) prior to analysis of organic compounds.
3. The titles above may change dependent on the assigned laboratories.

QAPP Worksheet #24
Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference ¹
GC/ MS	Initial Calibration and calibration verification check: Per laboratory SOP	After set up, prior to run and after instrument changes or failures of checks.	15 % RSD and not less than 30% for any compound; \pm 20% recovery per laboratory SOP.	Check, correct; re-calibrate and rerun all samples analyzed after last valid calibration check	Laboratory analyst / quality assurance (QA) officer - TBD	CAS SOP for PAH analysis: SOC-8270P, Rev. 7
	Calibration checks: continuing calibration verifications (CCVs) per laboratory SOP	Daily: Beginning of run and after every 10 samples and at end of analytical run	\pm 20% recovery per laboratory SOP.	Check, correct; re-calibrate and rerun all samples analyzed after last valid calibration check	Laboratory analyst / QA officer - TBD	
HRGC/ HRMS and HRGC/LRMS	Initial Calibration and calibration verification check: Per laboratory SOP	After set up, prior to run and after instrument changes or failures of checks.	% RSD and % recovery per laboratory SOPs.	Check, correct; re-calibrate and rerun all samples analyzed after last valid calibration check	Laboratory analyst / QA officer - TBD	Axys SOP for PAH analysis: MLA-021
	Calibration checks: CCVs per laboratory SOP	Daily: Beginning of run and after every 10 samples and at end of analytical run	% recovery per laboratory SOP	Check, correct; re-calibrate and rerun all samples analyzed after last valid cal check	Laboratory analyst / QA officer - TBD	EPA 1668A/ Axys SOP MSU-020 Axys SOP for Chlorinated pesticides by EPA 1613B Mod: MLA-035 Axys SOP for PCDD/ PCDF by EPA 1613B: MLA-017

QAPP Worksheet #24
Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference ¹
GC/MS SW-846 8270C	Initial calibration:	On award of contract, or corrective action which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement, etc.), or if the continuing calibration acceptance criteria have not been met.	relative response factor (RRF) \geq minimum acceptable RRF listed in Table 5 of procedure; All target compounds, initial relative standard deviation (RSD) \leq 10% or 20% and correlation coefficient (r) $>$ 0.995. %RSD \leq value in laboratory SOP.	Inspect system for problems (e.g., clean ion source, change the column, service the purge and trap device), correct problem, re-calibrate.	Laboratory GC/MS Technician	CAS SOP for PAH analysis: SOC-8270P, Rev. 7
GC/MS	Continuing calibration (CCV)	Once every 12 hours or as per laboratory SOPs	Percent difference (%D) \leq 15% or $<$ 30% or as per laboratory SOPs	Inspect system; correct problem; recalibrate the instrument, reanalyze affected samples and standards.	Laboratory GC/MS Technician	
GC/MS	Calibration Standards Verification	Each lot of standards	As per laboratory established control limits	Inspect system; correct problem; re-run standard and affected samples	Laboratory GC/MS Technician	CAS SOP for PAH analysis: SOC-8270P, Rev. 7
GC/MS	Tuning	Daily: every 12 hours	Response factors and RRF as method specified	Inspect system; correct problem; re-run standard and affected samples	Laboratory GC/MS Technician	
CVAFS	Per method and laboratory SOP	Calibration	Per method/ laboratory SOP. ICAL \leq 15% RSD.	Inspect the system, correct problem, re-calibrate, and re-analyze samples.	Assigned laboratory personnel	EPA 1630/1631
		ICV: Check daily when instrument is in use	85-115% R for Total mercury; 80-120% R for methyl mercury			Subcontract Microbac SOPs: Methyl Mercury Draft, Revision 0 and Hg-1631, Revision 2
		CCV: Beginning and after every 10 samples	77-123% R for total mercury; 67-133% R for methyl mercury			

QAPP Worksheet #24
Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference ¹
Inductively coupled plasma – mass spectrometry (ICP-MS)	See Shealy's SOP S-IM-021; as per instrument manufacturer's recommended procedures	Initial calibration: daily and each time the instrument is set up. Verify performance daily or once QC checks are non-compliant	$r \geq 0.998$; minimum of 3 standards and a blank.	Inspect the system, correct problem, re-calibrate, and re-analyze samples.	TBD Laboratory or Subcontractor ICP-MS Technician/analyst / QA officer	SW-846, 6020 Shealy SOPs S-IM-021, Revision 2
	Instrument performance check	Daily; after tuning and optimizing instrument	RSD < 5% after at least 4 runs of the tuning solution	Repeat analysis; re-prepare calibration standards and reanalyze		
	Initial calibration check - ICV	Before sample analysis	90-110% recovery; source of standard separate from calibration standards	Re-calibrate instrument; prepare fresh ICV standards; do not analyze samples until problem is fixed		
	Low Level ICV Standard	After initial calibration verification standard	70-130% recovery (concentration $\pm 30\%$ of true value); prepared from calibration standards			
	Continuing calibration check (CCV)	Every 10 samples and at end of analytical sequence	90-110% recovery; mid range of ICV standard	Find problem; re-calibrate and rerun all samples analyzed after last valid CCV		
	Low Level CCV Standard	Beginning and end of run; 10% frequency or every 2 hours during an analysis run	70-130% recovery; prepared from calibration standards			

Notes:

1. General GC/MS calibration requirements are presented. Instruments used for analyses follow the calibration frequencies outlined in the method SOPs (Appendix K of the Oversight QAPP, Addendum No. 5) and Appendix M of this Final QAPP Addendum No. 8. Laboratory specific calibration information is maintained by the laboratories; method specific calibration information is detailed in the methods.

QAPP Worksheet #28-a
QC Samples Table

Matrix	Aqueous					
Analytical Group	PAHs and Alkylated PAHs					
Concentration Level	Low					
Sampling SOP(s)	See Worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	Laboratory SOP, MLA-021					
Sampler's Name	TBD					
Field Sampling Organization	CDM					
Analytical Organization	Axys Analytical Services Ltd.					
No. of Sample Locations	See Worksheet #18 & 20					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	per extract batch	Per laboratory SOP	Investigate and correct per laboratory SOP	Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
MS/MSD and laboratory duplicate	1 per 20 samples	Per laboratory SOP	Investigate and correct; reanalyze affected samples. Flag outliers	Laboratory Analyst	Precision	± 20% of mean if sample concentration >10x DL
Matrix Spike	1 per 20 samples or with each group of field samples	Per laboratory SOP	Investigate and correct. Document in data summary	Laboratory Analyst	Accuracy	50-200% Recovery per laboratory SOP Table 2
Surrogate	Every field and QC sample, standards, blanks	Per laboratory SOP	Identify source of problem, make other adjustments and reanalyze	Laboratory Analyst	Accuracy	15-130% Recovery - See Laboratory SOP Table 2
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM analytical services coordinator (ASC)	Precision	≤ 40% RPD (for results ≥ 5*QL) or ABS<QL
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	Laboratory Analyst	Accuracy/representativeness	≤ 10 degrees Celsius for data validation

Notes:

The assigned laboratory also must perform the QA/QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs, such as laboratory duplicates and matrix spike duplicates for precision, matrix spikes, Deuterated monitoring compounds for accuracy, and blanks and method detection limits for sensitivity. The laboratory personnel must follow all the corrective actions required by the laboratory SOP.

QAPP Worksheet #28-b
QC Samples Table

Matrix	Aqueous					
Analytical Group	Chlorinated Pesticides					
Concentration Level	Low					
Sampling SOP(s)	See Worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	EPA 1613B Modified/ MLA-028 (MLA-035 Full SOP, Rev. 2, June 2010)					
Sampler's Name /Sampling Organization	TBD /CDM					
Analytical Organization	Axys Analytical Services Ltd.					
No. of Sample Locations	See Worksheet #18 & 20					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	per extract batch	<QL	Investigate and correct per laboratory SOP	Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
Laboratory Duplicate	1 per 20 samples	Per laboratory SOP	Investigate/correct; Flag outliers		Precision	± 20% of mean if sample concentration >10x DL
Initial Calibration	Prior to sample analysis	Per laboratory SOP	Investigate and correct		Accuracy	Per laboratory SOP
Calibration Verification/ Certified Reference Material	Beginning of each 12-hour shift; Periodically at least quarterly	Per laboratory SOP	Check standards; recalibrate if required			Tables 4 and 5 of laboratory SOP/ CRM-TBD
Ongoing Precision and Recovery/ MS	1 per batch of 20 samples prior to sample analysis	50-130% Recovery	Identify source of problem, make other adjustments as per laboratory SOP	Laboratory Analyst	Accuracy	See method limits; for individual compound limits see Tables 4 and 5 of laboratory SOP
Surrogate	Every field and QC sample, standards, blanks	30-200% Recovery	Evaluate data for interferences and apply corrective action as per SOP MLA-028 (full SOP not available)			
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	Laboratory Analyst	Accuracy/ representativeness	≤ 10 degrees Celsius for data validation

Notes:

1. The assigned laboratory also must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in EPA Method 1613B and laboratory SOP; such as performance of initial and ongoing studies, calibration verification, addition of internal standards, analyses of blanks and determination of detection limits.
2. The DLs referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits.

QAPP Worksheet #28-c
QC Samples Table

Matrix	Aqueous					
Analytical Group /Concentration Level	PCB Congeners/ Low (pg/L)					
Sampling SOP(s)	See Worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	EPA 1668A (MLA-010 Full SOP, Rev. 2, June 2010)					
Sampler's Name	TBD					
Field Sampling Organization	CDM					
Analytical Organization	EPA Headquarters Laboratory					
No. of Sample Locations	See Worksheets #18 & 20					
QC Sample:	Frequency/ Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per 20 samples	Concentration < 2 pg, 10 pg or 50 pg/sample-See SOP Table 1. Sum of all congeners < 300 pg /sample unless sample concentrations > 10* blank levels	If samples non-detect or if lowest sample result is >10 times the blank-no action; otherwise redigest and reanalyze	Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
Analysis (Laboratory) Duplicate	1 per 20 samples	± 20%mean for concentrations >10*QL	Flag outliers	Laboratory Analyst	Precision	RPD ≤ 20% for concentrations >10x DL ¹ ; otherwise ABS<QL
Certified Reference Material or Quality Control Sample	Periodically at least quarterly	70-130%R;	Check standards; recalibrate if required	Laboratory Analyst	Accuracy	70-130%R;
Calibration Verification Sample	Beginning of each 12-hour shift	70-130%R;	Adjust and/or recalibrate	Laboratory Analyst	Accuracy/bias	70-130%R
Initial Precision and Recovery	Prior to sample analysis	Per laboratory SOP	Investigate and correct	Laboratory Analyst	Accuracy	60-140%R ≤ 40% RSD
Ongoing Precision and Recovery	1 per batch of 20 samples	Per laboratory SOP	Identify source of problem, recalibrate if needed/ make other adjustments and reanalyze	Laboratory Analyst	Accuracy	Warning 70-130%R; Accept 50-150%R
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	RPD ≤ 40%; ABS<QL for samples <5x QL
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	Laboratory Analyst	Accuracy/ representativeness	≤ 10 degrees Celsius for data validation

1. The DLs referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits.

QAPP Worksheet #28-d
QC Samples Table

Matrix	Aqueous					
Analytical Group	PCDD/PCDF					
Concentration Level	Low (µg/L)					
Sampling SOP(s)	See Worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	EPA 1613B/ MLA-017 (MSU-018, Rev 5, June 2005)					
Sampler's Name	TBD					
Field Sampling Organization	CDM					
Analytical Organization	Axys Analytical Services Ltd.					
No. of Sample Locations	See Worksheet #18 & 20					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per 20 samples	TCDD/F <0.5 pg/sample, PeCDD/F, HxCDD/F, HpCDD/F <1.0 pg/sample, OCDD/F <5 pg/sample unless sample concentrations > 10* blank levels (per SOP)	If samples non-detect or if lowest sample result is >10 times the blank-no action; otherwise redigest and reanalyze	Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
Laboratory Duplicate	1 per 20 samples	± 20% mean for concentrations >10*QL	Investigate and correct; Flag outliers	Laboratory Analyst	Precision	± 20% of mean if sample concentration >10x DL ²
Initial Precision and Recovery	Prior to sample analysis	Per laboratory SOP, Table 1	Investigate and correct	Laboratory Analyst	Accuracy	Per method/laboratory SOP
Ongoing Precision and Recovery	1 per batch of 20 samples	Per laboratory SOP, Table 1 (70-130%R)	Identify source of problem, make other adjustments; redigest if needed and reanalyze	Laboratory Analyst	Accuracy	Individual laboratory established limits per SOP
Sample splits and field duplicates	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
MS/MSD	1 per 20 samples	±20% RPD	Investigate and correct	CDM ASC	Precision	±20% RPD
Surrogates	1 per 20 samples	40-120%R-warning limit 21-130%R-control limit		Laboratory Analyst	Accuracy/bias	40-120%R-warning limit 21-130%R-control limit
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	Laboratory Analyst	Accuracy/representativeness	≤ 10 degrees Celsius for data validation

Notes:

1. The assigned laboratory also must perform and meet all the measurement performance criteria that assess the analytical DQIs as specified in EPA Method 1613B.
2. The DLs referenced in the laboratory SOP are equivalent to the QLs or sample reporting limits

QAPP Worksheet #28-e
QC Samples Table

Matrix	Aqueous (Total and dissolved)					
Analytical Group /Concentration Level	TAL inorganic Metals / Low/Medium (µg/L)					
Sampling SOP(s)	See Worksheet #21– split of CPG samples					
Analytical Method/SOP Reference	SW-846, Method 6020 – Lab SOP S-IM-021 (Revision 2, May 2011)					
Sampler's Name	TBD					
Field Sampling /Analytical Organization	CDM / Shealy Environmental					
No. of Sample Locations	See Worksheet #20 and 18					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Splits and Field Duplicate	1 per 20 samples	None	Notify PM and address in data quality assessment	CDM ASC and PM	Precision	40% RPD for results ≥5QL
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note in laboratory narrative. CDM will check packing procedure and increase coolant	CDM field task leader (FTL)	Accuracy/representativeness	≤ 10 degrees Celsius
Field Equipment Blank	1 per sampling event	≤ QL	Verify results; re-analyze. Flag outliers. Check decontamination procedures.	Laboratory analyst / CDM PM	Accuracy / Contamination	≤ QL
Preparation Blank	1 per 20 samples	No constituent > QL	Suspend analysis fix source; redigest and reanalyze affected samples (see lab SOP)	Laboratory inductively coupled plasma (ICP) analyst	Accuracy	No constituent > QL
Matrix Spike	1 per 20 samples/event	75-125%R*	Flag outliers and run post digestion spike or dilution test	Laboratory ICP analyst	Accuracy	75-125%R*
Laboratory Duplicate or MS	1 per 20 samples	± 20% RPD**	Flag outliers	Laboratory ICP analyst	Precision	± 20% RPD**
Post-Digestion Spike	If serial dilution fails criteria	80-120%R	Flag outliers and run dilution test	Laboratory ICP analyst	Accuracy	75-125%R
Serial dilution test (1:5)	1 per batch	Dilution result ±10% of original when original result >10QL	Note chemical or physical interference effect in narrative	Laboratory ICP analyst	Accuracy	Dilution result ±10% of original result
Interference Check Sample	Beginning of run and /or every 12 hours	20% or 50% of true value (see lab SOP)	Check calculations and instruments, reanalyze affected samples (see lab SOP)	Laboratory ICP analyst	Sensitivity	± 2 times QL of true value or ± 20% of true value, whichever is greater
Laboratory Control Sample	1 per 20 samples	80-120%R	Re-run once; then redigest and reanalyze affected samples once	Laboratory ICP analyst	Accuracy	80-120%R

Notes:

* and ** except when the sample concentration is greater than 10 times the IDL, then disregard the recoveries; no data validation action taken

** - (include absolute difference criteria)

**except when the sample and/or duplicate concentration is less than 5 times the CRQL, then ± CRQL.

QAPP Worksheet #28-f
QC Samples Table

Matrix	Aqueous					
Analytical Group	Mercury (Total and dissolved)					
Concentration Level	Low/Medium (µg/L)					
Sampling SOP(s)	See worksheet #21– split of CPG samples					
Analytical Method/SOP Reference	EPA 1631 – Atomic fluorescence spectroscopy (SOP Hg-1631(2))					
Sampler's Name	TBD					
Field Sampling Organization	CDM					
Analytical Organization	Microbac					
No. of Sample Locations	See worksheet #20 and 18					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits*	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Sample splits and Field Duplicate	1 per 20 samples	20% RPD	Notify PM and address in data quality report	CDM ASC and PM	Precision	≤ 40% RPD (for results ≥ 5QL) or ABS≤QL
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note in laboratory narrative. CDM will use more coolant; check packing procedure	CDM FTL	Accuracy/representativeness	≤ 10 degrees Celsius for data validation
Field Rinsate Blank	1 per decontamination event not to exceed 1 per day	≤ QL	Verify results; re-analyze. Flag outliers. Check decontamination procedures.	Laboratory analyst / CDM PM	Accuracy / Contamination	≤ QL
Preparation Blank (PB)	1 per 20 samples	No analyte > QL (greater of 0.4 ng or <0.1xsample)	Suspend analysis; redigest and reanalyze if sample<10*blank result	Laboratory Analyst	Accuracy	No analyte > QL
Laboratory duplicate	1 per 20 samples	Per laboratory SOP	Investigate and correct; Flag outliers; Note in case narrative. Multiple failures require re-distillation and reanalysis.		Precision	≤ 35% RPD if result >5QL
Certified Reference Material (Quality Control Sample) or Ongoing Precision and Recovery Samples	1 per 20 samples or 12-hour shift	Per laboratory SOP	Check calculations and instruments, reanalyze affected samples. Report in case narrative.		Accuracy/Precision	70-130%R for OPR/CRM <20 RSD for IPR 75-125%R for IPR
MS/MSD	1 per 20 samples or with each group of field samples	Per laboratory SOP	Investigate matrix effects and note in data narrative.		Accuracy	70-130%R
					Precision	RPD ≤35% (30 per method)

Notes:

*- The laboratory SOP references the limits in the Laboratory Information Management System (LIMS) which are the internal laboratory control limits.

QAPP Worksheet #28-g
QC Samples Table

Matrix	Aqueous					
Analytical Group /Concentration Level	Methyl Mercury (Total and dissolved) /Trace					
Sampling SOP(s)	See Worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	EPA 1630					
Sampler's Name	TBD					
Field Sampling Organization	CDM					
Analytical Organization	CDM Subcontract Laboratory - Microbac					
No. of Sample Locations	See Worksheet #18 & 20					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Sample splits and field duplicates	1 per 20 samples	RPD <35% (method 1630)	Data assessor to inform PM if MPC is exceeded; address in data quality assessment	CDM ASC	Precision	≤ 40% RPD (for results ≥ 5QL)
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note in laboratory narrative. CDM will use more coolant; check packing procedure	Laboratory Analyst	Accuracy/representativeness	≤ 10 degrees Celsius
Preparation Blank	1 per 20 samples or batch	< 0.0001 ng/L per method or Per laboratory SOP	Suspend analysis until source rectified; re-distill and reanalyze affected samples if results are <10 times the blank	Laboratory Analyst	Accuracy/Sensitivity	No result > QL
LCS	1 per 20 samples batch or per day	Per limits in LIMS	Stop analysis and recalibrate or report data with an appropriate qualifier. Document on CAR form.	Laboratory Analyst	Accuracy	Per limits in LIMS
Quality Control Sample	1 per 20 samples batch or 1 per day mid batch	Per laboratory SOP – or method Table 2	Investigate and correct; Flag outliers; Note in case narrative. Multiple failures require re-distillation and reanalysis.	Laboratory Analyst	Accuracy	Per laboratory SOP
Initial and Ongoing Precision and Recovery Samples	1 per 20 samples or group of field samples at end of run or 12-hour shift	Per laboratory SOP	Check calculations and instruments, recalibrate for IPR and reanalyze affected samples for OPR	Laboratory Analyst	Accuracy	77-123%R of true value for OPR 79-121%R for IPR per method
MS/MSD	1 per 20 samples or with each group of field samples	Per limits in LIMS	Investigate matrix effects and note in data narrative	Laboratory Analyst	Accuracy	75-125%R
					Precision	RPD ≤25%

Notes:

The assigned laboratory also must perform the QA/QC sample analyses and meet all the measurement performance criteria that assess the analytical DQIs as specified in the method or laboratory SOP and or subcontract Statement of work (SOW) as applicable.

QAPP Worksheet #28-h
QC Samples Table

Matrix	Aqueous					
Analytical Group	Hexavalent Chromium (Dissolved)					
Concentration Level	Low/Medium (mg/L)					
Sampling SOP(s)	See worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	SM 3500 Cr B DESA SOP C-96					
Sampler's Name	TBD					
Field Sampling Organization	CDM					
Analytical Organization	As per FASTAC [DESA or Subcontract Laboratory]					
No. of Sample Locations	See worksheet #20 and 18					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Preparation Blank (PB)/	1 per 20 samples	None	Suspend analysis; check; redigest and reanalyze	DESA or subcontract Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
Sample splits and Field Duplicate	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; flag duplicate results	CDM ASC	Precision	40% RPD
Laboratory Duplicate	1 per 20 samples	None	Flag outliers	DESA or subcontract Laboratory Analyst	Precision	40% RPD
Spike Samples	1 per 20 samples	None	Flag outliers	DESA or subcontract Laboratory Analyst	Accuracy	75 – 125 %R
Laboratory Control Sample	After calibration, every 20 samples and at end of day	None	Identify source of problem, recalibrate if needed/ make other adjustments and reanalyze	DESA or subcontract Laboratory Analyst	Accuracy	80-120%R
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Inform field crew of failure and need for additional coolant; check packing procedure	DESA or subcontract Laboratory Analyst	Accuracy/ representativeness	≤ 10 degrees Celsius for data validation

Notes:

Control limits for the LCS must be documented and provided.

QAPP Worksheet #28-i
QC Samples Table

Matrix	Aqueous					
Analytical Group	Wet Chemistry –TDS-Oven / Balance					
Concentration Level	Low/Medium (mg/L)					
Sampling SOP(s)	See worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	SM2540D (DESA SOP C-37 Modified)					
Sampler's Name	George Molnar or TBD					
Field Sampling Organization	CDM					
Analytical Organization	As per FASTAC [DESA or Subcontract Laboratory]					
No. of Sample Locations	See worksheet #20 and 18					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Preparation/ Method Blank	1 per batch of 20 samples	None	If samples non-detect or if lowest sample result is >10 times the blank-no action; otherwise reanalyze and qualify data	DESA	Accuracy/Sensitivity	No analyte > QL
Laboratory Duplicate	1/20 or per batch	Per laboratory SOP, ≤ 20 RPD	Flag outliers	DESA	Precision	≤ 20 RPD; ABS ≤QL for samples <5x QL
Sample splits and Field Duplicates	1 per 20 samples or per event	None	Data assessor to inform PM if MPC is exceeded; flag results in report	CDM ASC	Precision	≤20% RPD if > 5xQL otherwise ABS ≤QL
Laboratory Control Sample or Quality Control Sample	2 per batch of 20 samples	Average Recovery within the standard manufacture's limits or method limits; % RPD < 20	Identify source of problem, re-prepare and re-analyze or flag outliers	DESA	Accuracy	80-120%R or as stipulated stipulated by manufacturer or laboratory
Laboratory Control Sample or Quality Control Sample Duplicate				DESA	Precision	≤20% RPD
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	DESA	Accuracy/ representativeness	≤ 10 degrees Celsius for data validation

Notes:

Sample Splits performance criteria are outlined on Worksheet # 11.



QAPP Worksheet #28-j
QC Samples Table

Matrix	Aqueous					
Analytical Group	Wet Chemistry – TOC-Carbon analyzer + IR or FID detector					
Concentration Level	Low/Medium (mg/L)					
Sampling SOP(s)	See worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	SM5310B, DESA SOP C-83					
Sampler's Name	TBD					
Field Sampling Organization	CDM					
Analytical Organization	As per FASTAC [DESA or Subcontract Laboratory]					
No. of Sample Locations	See worksheet #20 and 18					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1 per 20 samples or less in extraction batch	< QL	If samples non-detect or if lowest sample result is >10 times the blank-no action; otherwise investigate source of contamination, redigest and reanalyze	DESA or subcontract Laboratory Analyst	Accuracy/Sensitivity	No analyte > QL
Laboratory Duplicate	All samples duplicated	≤ 20% RPD; ±QL for samples <5x QL	Flag outliers	DESA or subcontract Laboratory Analyst	Precision	40% RPD
Matrix Spike	1 per batch of 20 samples or less	80-120%R	Flag outliers	DESA or subcontract Laboratory Analyst	Accuracy	80-120%R
Laboratory Control Sample	2 per batch of 20 samples or less	Average Recovery meet standard manufacturer's limits; % RPD < 20	Identify source of problem, reanalyze, qualify data	DESA or subcontract Laboratory Analyst	Accuracy/Precision	Average Recovery meet standard manufacturer's limits; % RPD < 20
Sample splits and Field Duplicate	1 per 20 samples	None	Data assessor to inform PM if MPC is exceeded; flag duplicate results	CDM ASC	Accuracy	40% RPD
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Inform field crew of failure and need for additional coolant; check packing procedure	DESA or subcontract Laboratory Analyst	Accuracy/representativeness	≤ 10 degrees Celsius for data validation

Notes:

Control limits for the LCS must be documented and provided.

QAPP Worksheet #28-k
QC Samples Table

Matrix	Aqueous					
Analytical Group	Wet Chemistry – DOC-Carbon analyzer + IR or FID detector					
Concentration Level	Low (mg/L)					
Sampling SOP(s)	See worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	Standard Method 5310B (DESA SOP C-83 Modified)					
Sampler's Name	George Molnar or TBD					
Field Sampling Organization	CDM					
Analytical Organization	As per FASTAC [DESA or Subcontract Laboratory]					
No. of Sample Locations	See worksheet #20 and 18					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank /Calibration Blank	1 per 20 samples	< QL	If samples non-detect or if lowest sample result is >10 times the blank-no action; otherwise redigest /reanalyze. Flag results or modify reporting limit.	DESA	Accuracy/ Sensitivity	No analyte > QL
ICV/CCV	1 per batch of 10 samples	85-115%R	Suspend analysis, find cause, and reanalyze associated samples	DESA	Accuracy	85-115%R
Laboratory Duplicate	All samples duplicated	≤ 20% RPD if values >5QL; otherwise ABS≤5QL	Flag outliers	DESA	Precision	RPD ≤ 20% if values >5QL; otherwise ABS≤5QL
Matrix Spike	1 per batch of 20 samples	80-120%R	Flag outliers	DESA	Accuracy	80-120%R
LCS/ Quality Control Sample	1 per batch of 20 samples	80-120%R	Identify source of problem, recalibrate if needed/ make other adjustments and reanalyze or flag outliers	DESA	Accuracy	80-120%R or as stipulated stipulated by manufacturer or laboratory
LCS or Quality Control Sample Duplicate		RPD ≤ 20%			Precision	RPD ≤ 20%
Sample splits and Field Duplicates	1 per 20 samples or per event	None	Data assessor to inform PM if MPC is exceeded; flag results in report	CDM ASC	Precision	≤ 40% RPD if >5xQL; otherwise ABS≤QL
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure /need for additional coolant; check packing steps	DESA	Accuracy/ representativeness	≤ 10 degrees Celsius for data validation

Notes: Sample Splits performance criteria are outlined on Worksheet # 11.

QAPP Worksheet #28-I
QC Samples Table

Matrix	Aqueous					
Analytical Group	Wet Chemistry – POC-Carbon analyzer + IR or FID detector					
Concentration Level	Low (mg/L)					
Sampling SOP(s)	See worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	MCAWW EPA Method 415.1 (DESA SOP C-88 Modified)					
Sampler's Name	George Molnar or TBD					
Field Sampling Organization	CDM					
Analytical Organization	As per FASTAC [DESA or Subcontract Laboratory]					
No. of Sample Locations	See worksheet #20 and 18					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank /Calibration Blank	1 per batch of 20 samples or less	< QL	If samples non-detect or if lowest sample result is >10 times the blank-no action; otherwise redigest and reanalyze. Flag results or modify reporting limit.	DESA	Accuracy/Sensitivity	No analyte > QL
Laboratory Duplicate	All samples duplicated	Per DESA SOP	Flag outliers	DESA	Precision	RPD ≤ 20 if values >5xQL otherwise ABS ≤QL
ICV/CCV	ICV-prior to samples; CCV 1 per batch of 10 samples or every 12 hours	85-115%R	Suspend analysis, find cause, and reanalyze associated samples	DESA	Accuracy	90-110%R
Laboratory Control Sample/Analytical Quality Control	1 per batch of 20 samples or less	80-120%R or as supplier certified	Identify source of problem, re-prepare and re-analyze or flag outliers	DESA	Accuracy	80-120%R or as supplier certified
Laboratory Control Sample/Analytical Quality Control Duplicate		RPD ≤ 20%			Precision	RPD ≤ 20%
Sample splits and Field Duplicate	1 per 20 samples per event	None	Data assessor to inform PM if MPC is exceeded; flag results in report	CDM ASC	Precision	RPD ≤ 40% if >5xQL otherwise ABS ≤QL
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	DESA	Accuracy/bias	≤ 10 degrees Celsius for data validation

Notes: Sample Splits performance criteria are outlined on Worksheet # 11.

QAPP Worksheet #28-m
QC Samples Table

Matrix	Aqueous					
Analytical Group	Wet Chemistry – SSC (TSS)-Oven / Balance					
Concentration Level	Low/Medium (mg/L)					
Sampling SOP(s)	See worksheet #21 – split of CPG samples					
Analytical Method/SOP Reference	Standard Method 2540D (DESA SOP C-33 Modified)					
Sampler's Name	George Molnar or TBD					
Field Sampling Organization	CDM					
Analytical Organization	As per FASTAC [DESA or Subcontract Laboratory]					
No. of Sample Locations	See worksheet #20 and 18					
QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Preparation/ Method Blank	1 per batch of 20 samples	None	If samples non-detect or if lowest sample result is >10 times the blank-no action; otherwise reanalyze and qualify data	DESA	Accuracy/Sensitivity	No analyte > QL
Laboratory Duplicate	1/20 or per batch	Per laboratory SOP, ≤ 20 RPD	Flag outliers	DESA	Precision	≤ 20 RPD; ABS ≤ QL for samples <5x QL
Sample splits and Field Duplicates	1 per 20 samples or per event	None	Data assessor to inform PM if MPC is exceeded; flag results in report	CDM ASC	Precision	≤20% RPD if > 5xQL otherwise ABS ≤ QL
Laboratory Control Sample or Quality Control Sample	2 per batch of 20 samples	Average Recovery within the standard manufacture's limits or method limits; % RPD < 20	Identify source of problem, re-prepare and re-analyze or flag outliers	DESA	Accuracy	80-120%R or as stipulated stipulated by manufacturer or laboratory
Laboratory Control Sample or Quality Control Sample Duplicate				DESA	Precision	≤20% RPD
Temperature Blank	1 per cooler	≤ 6 degrees Celsius	Note outlier in laboratory narrative. Inform CDM of failure and need for additional coolant; check packing procedure	DESA	Accuracy/bias	≤ 10 degrees Celsius for data validation

Notes:

Sample Splits performance criteria are outlined on Worksheet # 11.



QAPP Worksheet #29
Project Documents and Records Table

Sample Collection Documents and Records	On-Site Analysis Documents and Records	Off-Site Analysis Documents and Records	Data Assessment Documents and Records	Other
FORMS II Lite Traffic Reports/ COC Records	No on-site analysis will be performed	Sample Receipt, Custody and Tracking Logs	Corrective Action Reports	Purchase Requisition Forms
Airbills	Logbook Notes	Standards Tracking Logs	Analytical sample results	Laboratory SOPs
Sample Tracking Log/Sheets	Photographs	Corrective Action Reports	Laboratory certifications	Technical/QA Review Forms
Field datasheets/logbooks	No on-site analysis will be performed	Corrective Action Forms	Laboratory QA Plan (on file with EPA and CDM)	ANSETS Report Forms
Daily Summary Report via e-mail		Data Packages (Case Narratives, Sample Results, QC Summaries and Raw Data (detailed in SOPs).	QC Audit Reports Data Validation SOPs Data Validation Reports	Telephone Logs
Field Change Request Forms		Trip Reports	Data Package Completeness Checklist Validated Data Reports	Electronic Data Deliverables
Custody Seals		Sample analysis run logs	Self Assessment Checklist	Non-Conformance Reports
ANSETS Forms		Sample Receipt, Custody and Tracking Logs		

QAPP Worksheet #30
Analytical Services Table

Matrix	Analytical Group	Concentration Level	Analytical SOP	Data Package Turnaround Time ^{1,3}	Laboratory/Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/Organization (Name and Address, Contact Person and Telephone Number)
	PAHs /Alkyl PAHs	Low	8270C Modified AxyS SOP MLA-021	Event 1 select locations Quick TAT for Group A analyses Other events 51 days (21 days /30 days)	AXYS Analytical Services Ltd. 2040 Mills Road West Sidney, BC V8L 5X2, Canada 1-888-373-0881	CAS Kelso
	Chlorinated pesticides	Low	AxyS SOP MLA-035			TBD
	PCDD/PCDF	Low	EPA 1613B/ AxyS SOP MLA-017			
	PCB Congeners	Low	EPA 1668A/ AxyS SOP MSU-020			
	TAL Metals	Low	ICP MS EPA 6020	Select Quick TAT Regular 65 days (35 days /30 days)	Shealy Environmental, Inc. 106 Vantage Point Drive West Columbia, SC 29172 Attention: Nisreen Saikaly 1-800-673-9375	TBD
	Mercury	Low	EPA 1631	65 days (35 days /30 days)	Microbac Laboratories, Inc. 250 West 84 th Drive Merrillville, IN 46410 Attention: Kevin Falvey 219-769-8378	TBD
	Methyl mercury	Low	EPA 1630			
	Hexavalent Chromium	Low	SM 3500 Cr B (DESA SOP C-96) ²	65 days (35 days /30 days)	DESA Primary contact: RSCC Adly Michael/Bob Toth 732-906-6161/6171 DESA contact: John Birri 732-906-6886	Master Services Agreement Subcontract Laboratory (TBD)
	TDS	Low	SM 2540D (DESA SOP C-37 Modified)			
	TOC	Low	SM5310B (DESA SOP C-83)			
	Suspended Solids (TSS)	Low	SM2540D (DESA SOP C-33 Modified)			
	DOC	Low	SM 5310B (DESA SOP C-83 Modified)			
	POC	Low	SM 5310B/ 415.1 (DESA SOP C-88 Modified)			

Notes:

- Subcontract laboratories will communicate with the ASC on split sample status and potential analytical difficulties (if any arise). With the approval of the ASC and Task Leader, the turn-around-time for the laboratory data package deliverable can be adjusted to account for re-analysis or additional quality control as necessary.
- DESA currently SOP is C-96, which is based on HACH Method 8023. However, to match the CPG's method CDM will request EPA Method 218.6.
- Event 1, Routine Sampling Event split samples will target the EPA pre-selected locations with a rapid analytical turnaround of Group A parameters. Other split samples will be shipped with regular turnaround times.

QAPP Worksheet #36
Validation (Steps IIa and IIb) Summary Table

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria ^{1,2}	Data Validator (title and organizational affiliation)
IIa /IIb	Aqueous	PAHs – 8270C	Low	National Functional Guidelines	CDM ASC, Scott Kirchner or designee
IIa /IIb		PAH and Alkyl PAHs	Low	National Functional Guidelines	
IIa /IIb		Chlorinated pesticides	Trace/Low	National Functional Guidelines	
IIa /IIb		PCDD/PCDF	Low	EPA SOP HW-19 or 25, Validating PCDD/PCDF by HRGC/HRMS, Revision 1 or National Functional Guidelines	
IIa /IIb		PCB Congeners	Low	Data Validation Guidelines SOP HW-46, rev 0 or National Functional Guidelines	
IIa /IIb		TAL Metals	Low	Region 2 - Data Validation Guidelines SOP HW-2, rev 13 or National Functional Guidelines	
IIa /IIb		Mercury	Low/Medium	National Functional Guidelines modified by QAPP Worksheets 12,15,,19 and 24	
IIa /IIb		Methylmercury	Trace	National Functional Guidelines modified by QAPP Worksheets #12,15,19 and 24	
IIa /IIb		Hexavalent Chromium	Low	DESA validation SOP – Data evaluation will review against QAPP measurement performance criteria	DESA
IIa /IIb		TDS	Low		
IIa /IIb		TOC	Low		
IIa /IIb		DOC	Low		
IIa /IIb		POC	Low		
IIa /IIb		TSS/ Suspended Solids Concentration	Low		

Notes:

1. DESA laboratory results will be validated by EPA staff.
2. Subcontract laboratory results will be validated by the process of data verification and assessment utilizing the laboratory QC summaries.
3. All validation procedures will utilize the measurement performance criteria in the QAPP and any additional method requirements.

QAPP Worksheet #37
Usability Assessment

The Data Comparability Report will be prepared by CDM personnel. Frank Tsang, Task Order Manager, will be responsible for its content and for assigning work to the CDM personnel who will be supporting this assessment. The data comparability review and usability assessment will be conducted on validated data. The effectiveness of control actions will be evaluated during the laboratory review of the data, data validation and data evaluation and data quality assessment process. Data information will be documented in the laboratory narrative, data validation report and in the Data Comparability Report. The report will include an overall assessment of the CPG's analytical data using the results of the split sampling and field oversight including the field oversight observations of deficiencies and compliance; and an assessment of the split sampling data quality. The following items will be assessed for CDM split samples and conclusions drawn based on their results:

Precision – Split samples will be compared using the RPD for each pair of results reported above QL. As appropriate, alternative data comparisons will be used. If needed, other statistical determination may be conducted consistent with the Newark Bay split samples collected by Louis Berger. Additional information on data handling is included on Worksheet #11 under the section titled "What will the Data be Used for".

Results of laboratory duplicates will be assessed during data validation and data will be qualified according to the data validation procedures cited on Worksheet #36. RPD acceptance criteria of less than or equal those listed in this QAPP will be used to assess sampling precision. Absolute difference will be used when one or both results are at or below the QL. An absolute difference of less than five times the QL will be the acceptance criteria. A discussion summarizing the results of laboratory precision and any limitations on the use of the data will be described in the report.

Accuracy/Bias Contamination – Results for all laboratory blanks will be assessed as part of the data validation. During the validation process, the validator will qualify the data following the procedures described on Worksheet #36. A discussion summarizing the results of laboratory accuracy and bias based on contamination will be presented and any limitations on the use of the data will be described in the report.

Overall Accuracy/Bias – The results of instrument calibration and surrogate spike recoveries will be reviewed and data will be qualified according to the data validation procedures cited on Worksheet #36. A discussion summarizing the results of laboratory accuracy and any limitations on the use of the data will be described in the report.

Sensitivity – Data results will be compared to project action limits provided on Worksheet #15. A discussion summarizing any conclusions about sensitivity of the analyses will be presented, and any limitations on the use of the data will be described in the report.

Representativeness – A review of adherence to field procedures and of project QA audits will be performed in order to assess the representativeness of the sampling program. Data validation narratives will also be reviewed, and any conclusions about the representativeness of the data set will be discussed.

QAPP Worksheet #37
Usability Assessment

Comparability – The results of this study will be used in conjunction with the CPG’s data to support the investigation results. The data will be collected, analyzed and reported in a manner that is comparable to the CPG’s data set. The RPD between CDM’s and the CPG’s data will be calculated.

Completeness – A completeness check will be done on analytical data generated by the laboratories. Completeness will be calculated for each analyte and compared to the project completeness goal of 90 percent. For sampling, completeness will be calculated as the number of samples collected and analyzed divided by the number of planned for collection. For each analyte, completeness will also be calculated as the number of data points that meet measurement performance criteria divided by the total number of data points for that analyte. A discussion summarizing the results of project completeness and any limitations on the use of the data will be described in the report.

Reconciliation – The PQLGs presented in Worksheet #12 will be examined to determine if the objectives were met. This examination will include a combined overall assessment of the results of each analysis pertinent to an objective. Each analysis will first be evaluated separately in terms of major impacts observed from data validation, data quality indicators and measurement performance criteria assessments. Based on the results of these assessments, the quality of the data will be determined. Based on the quality determined, the usability of the data for each analysis will be determined. Based on the combined usability of the data from all analyses for an objective, it will be determined if the PQLG was met and whether project goals were achieved. As part of the reconciliation of each objective, conclusions will be drawn and any limitations on the usability of any of the data will be described.

The following equations will be used:

1. To calculate split sample precision:

$$RPD = 100 * 2 |X1 - X2| / (X1 + X2)$$

where X1 and X2 are the reported concentrations for CPG’s sample and CDM split sample /field duplicate

2. To calculate split data completeness:

$$\% \text{ Completeness} = V/n * 100 \quad - \text{ where } V = \text{ number of measurements judged valid; } n = \text{ total number of measurements made and}$$

$$\% \text{ Completeness} = C/x * 100 \quad - \text{ where } C = \text{ number of samples collected; } x = \text{ total number of measurements planned}$$

The investigation results will be presented in table and figures and in the text of the Data Comparability Report. Data gaps will be evaluated if requested by USACE/EPA. The report will discuss the completeness of the planned and collected data and the affect on the data objective of evaluating the accuracy of the CPG’s data.

References:

CDM Federal Programs Corporation (CDM). 2010. *Final Quality Assurance Project Plan Physical Water Column Monitoring and Generic Information for Upcoming Tasks*. March 10.

AECOM. 2011. Lower Passaic River Restoration Project. Lower Passaic River Study Area RI/FS. *Quality Assurance Project Plan/Field Sampling Plan Addendum. Remedial Investigation Water Column Monitoring/Small Volume Chemical Data Collection*. Revision 1. July 2011.

Louis Berger Group. 2011. Lower Passaic River Restoration Project. Draft *Oversight Quality Assurance Project Plan for Water Column Monitoring in the Newark Bay Study Area*. May 10.

Appendix M
Lower Passaic River Restoration Project
Chemical Water Column Monitoring Study/
Small Volume Data Collection

Figure 1

Excerpted from CPG's QAPP Field Sampling Plan dated July 2011

August 2, 2011

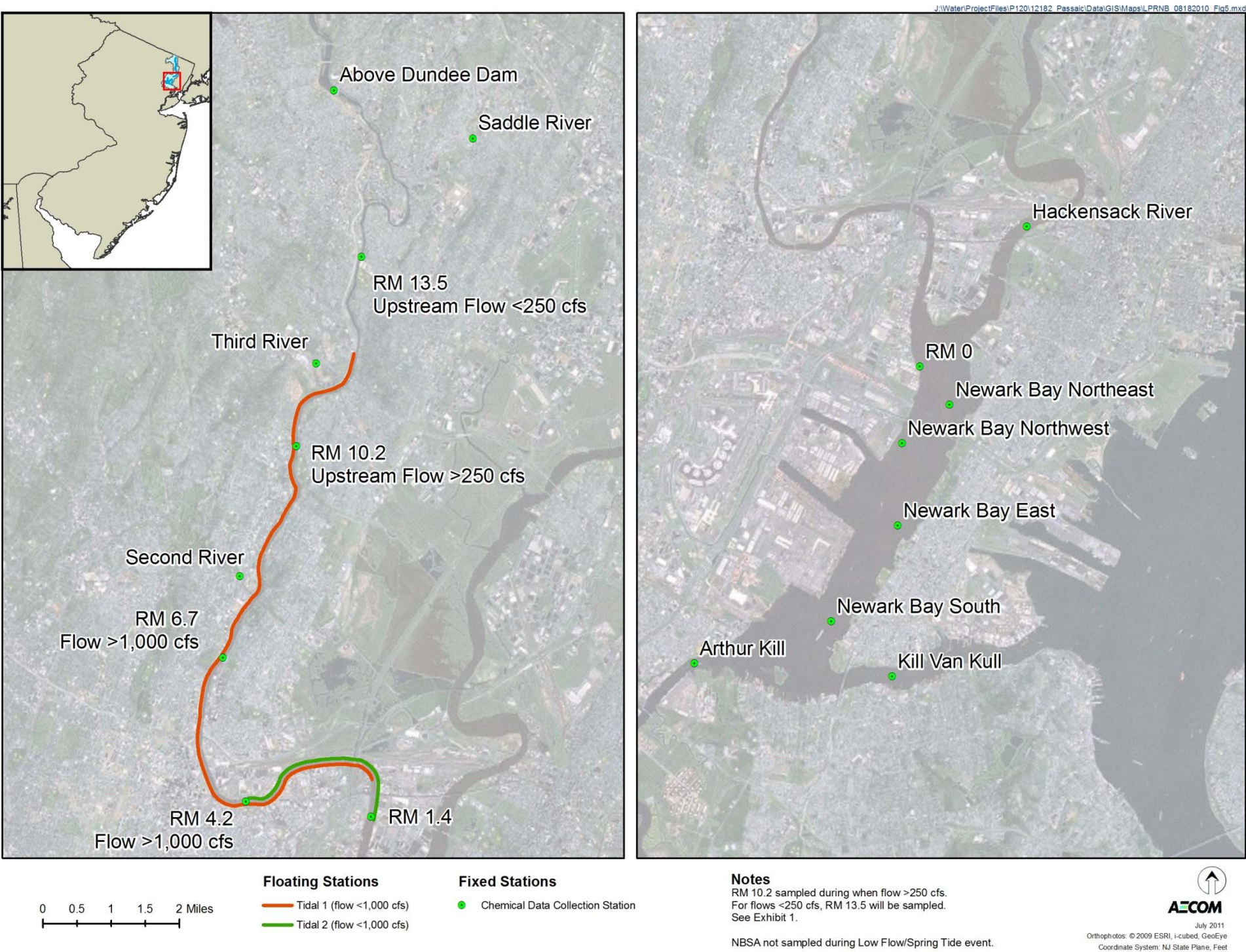


Figure 1: CWCM Program Sampling Locations

Appendix N

Laboratory SOPs

PAH / Alkyl PAH	AXYS
Chlorinated Pesticides	AXYS
PCB Congeners	AXYS
PCDD/PCDF	AXYS
TAL Metals	Shealy
Mercury	Microbac
Methyl mercury	Microbac
Hexavalent Chromium	DESA
TSS	DESA

Appendix N
Laboratory SOPs

AXYS SOP
MLA-021, Revision 10.2 Summary

Polycyclic Aromatic Hydrocarbons (PAHs) and Alkylated
PAHs (Alkyl PAH)
By EPA 8270C/D

Summary of AXYS Method MLA-021 Rev 10.02:

ANALYTICAL METHOD FOR THE DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH), ALKYLATED POLYCYCLIC AROMATIC HYDROCARBONS, AND ALKANES

AXYS Method MLA-021 describes the determination of concentrations of PAHs, alkylated PAHs and alkanes in solid (sediment, soil, ash), tissue (including blood), aqueous, XAD-2 column (resin and filters), air, and oil samples and in solvent extracts.

The method may be used for analysis of samples where USEPA Methods 1625B or 8270C/D have been requested **provided the modifications described in this document are permitted by contract.**

This summary document covers only the analysis of PAHs and alkylated PAHs.

Target Analytes

PAHs and alkylated PAHs determined by multi-point calibration

PAHs

Naphthalene	Benzo(b)fluoranthene
Acenaphthylene	Benzo(j/k)fluoranthenes
Acenaphthene	Benzo(f)fluoranthene
Fluorene	Benzo(e)pyrene
Phenanthrene	Benzo(a)pyrene
Anthracene	Perylene
Fluoranthene	Dibenzo(ah)anthracene
Pyrene	Indeno(1,2,3-cd)pyrene
Benz(a)anthracene	Benzo(ghi)perylene
Chrysene	

Alkylated PAHs

1-Methylnaphthalene	9/4-Methylphenanthrenes
2-Methylnaphthalene	2-Methylantracene
C1-Naphthalenes	C1-Phenanthrenes/Anthracenes
1,2-Dimethylnaphthalene	1,7-Dimethylphenanthrene
2,6-Dimethylnaphthalene	1,8-Dimethylphenanthrene
C2-Naphthalenes	2,6-Dimethylphenanthrene
2,3,5-Trimethylnaphthalene	3,6-Dimethylphenanthrene
2,3,6-Trimethylnaphthalene	C2-Phenanthrenes/Anthracenes
C3-Naphthalenes	1,2,6-Trimethylphenanthrene
1,4,6,7-Tetramethylnaphthalene	C3-Phenanthrenes/Anthracenes
C4-Naphthalenes	Retene
1-Methylphenanthrene	C4-Phenanthrenes/Anthracenes
2-Methylphenanthrene	Biphenyl
3-Methylphenanthrene	Dibenzothiophene

PAHs and alkylated PAHs determined by single-point calibration

C1-Biphenyls	C1-Fluoranthenes/Pyrenes
C2-Biphenyls	C2-Fluoranthenes/Pyrenes
C1-Acenaphthenes	C3-Fluoranthenes/Pyrenes
2-Methylfluorene	C4-Fluoranthenes/Pyrenes
C1-Fluorenes	1-Methylchrysene
1,7-Dimethylfluorene	5/6-Methylchrysenes
C2-Fluorenes	C1-Benz(a)anthracenes/Chrysenes
C3-Fluorenes	5,9-Dimethylchrysene
2/3-Methyldibenzothiophenes	C2-Benz(a)anthracenes/Chrysenes
C1-Dibenzothiophene	C3-Benz(a)anthracenes/Chrysenes
2,4-Dimethyldibenzothiophene	C4-Benz(a)anthracenes/Chrysenes
C2-Dibenzothiophene	7-Methylbenzo(a)pyrene
C3-Dibenzothiophene	C1-Benzofluoranthenes/Benzopyrenes
C4-Dibenzothiophene	C2-Benzofluoranthenes/Benzopyrenes
3-Methylfluoranthene/Benzo(a)fluorene	

EXTRACTION

All samples are spiked with deuterated surrogate standards prior to extraction and extracted as per the table below. Optional extraction procedures are shown within parentheses.

Sample Extraction

Matrix	Extraction
Aqueous	No particulate - Liquid-liquid extraction with dichloromethane. Visible particulate - sample is filtered prior to extraction and the particulate fraction separately extracted by Soxhlet extraction with dichloromethane. The two extracts are then combined.(Optional: the filtrate can be added to the extraction solvent for the particulate)
Solid (sediment, soil, sludge, particles on filter paper)	Soxhlet extraction with dichloromethane (Optional: Base digestion and liquid-liquid extraction with hexane)
Solid (ash)	Soxhlet extraction with toluene
Solid (fly ash)	Sonication with hydrochloric acid and filtering. Liquid-liquid extraction of filtrate using dichloromethane, Soxhlet extraction of particulate using toluene:acetone 80:20. The two extracts are combined.
Tissue	Base digestion and liquid-liquid extraction with hexane (Optional: Soxhlet extraction with dichloromethane, this option is not recommended for samples with high lipid content)
Whole blood/serum	Liquid-liquid extraction with ethanol:hexane:saturated ammonium sulphate.
XAD-2 column and filter	XAD-2 columns and filters are usually co-extracted for multiple analyses (For example: PCB, dioxins, pesticides) and the resulting extracts are split with a portion being used for PAH analysis
Ambient air (PUF and filter)	The PUF and filter(s) are Soxhlet extracted together using dichloromethane

Stationary Source Air Samples (Stack Gas sample trains)	The filter is sonicated with dilute hydrochloride acid and filtered. Equipment rinsates are collected, filtered, dried and/or extracted depending on sampling conditions.
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COLUMN CHROMATOGRAPHY CLEANUP

Extracts are routinely cleaned up using the following procedures:

- column chromatography on Silica
- gel permeation (Biobeads) column chromatography
- treatment with activated copper (except tissues)

Extracts may be cleaned up further, as necessary, using some or all of the following procedures:

- washing with base
- column chromatography on Biobeads
- column chromatography on alumina

INSTRUMENTAL ANALYSIS

Instrumental analysis is performed by low-resolution mass spectrometry (LRMS) using an RTX-5 capillary GC column. The LRMS is operated at a unit mass resolution in the electron impact (EI) ionization mode using multiple ion detection (MID) acquiring at least one characteristic ion for each target analyte and surrogate standard.

Analyte Ions Monitored, Surrogates Used and RRF Determination For PAH

TARGET ANALYTES	Quantification Ion (m/z)	Confirmation Ions (m/z)	Typical Ion Ratio (Conf./Quant.)	SURROGATE	Typical Retention Time (minutes)	RRF DETERMINED FROM
Naphthalene	128	102	0.064	d ₈ -Naphthalene	6.84	Naphthalene
Acenaphthylene	152	151	0.222	d ₈ -Acenaphthylene	10.83	Acenaphthylene
Acenaphthene	154	153	1.18	d ₈ -Acenaphthylene	11.33	Acenaphthene
Fluorene	166	165	1.01	d ₁₀ -Phenanthrene	12.63	Fluorene
Phenanthrene	178	176	0.202	d ₁₀ -Phenanthrene	15.04	Phenanthrene
Anthracene	178	176	0.196	d ₁₀ -Phenanthrene	15.15	Anthracene
Fluoranthene	202	200	0.214	d ₁₀ -Fluoranthene	18.06	Fluoranthene
Pyrene	202	200	0.219	d ₁₀ -Fluoranthene	18.60	Pyrene
Benz[a]anthracene	228	226	0.281	d ₁₂ -Benz[a]anthracene	21.68	Benz[a]anthracene
Chrysene ¹	228	226	0.312	d ₁₂ -Chrysene	21.79	Chrysene
Benzo[b]fluoranthene	252	253	0.218	d ₁₂ -Benzo[b]fluoranthene	25.21	Benzo[b]fluoranthene
Benzo[j,k]fluoranthenes	252	253	0.215	d ₁₂ -Benzo[k]fluoranthene	25.30	Benzo[k]fluoranthene
Benzo[e]pyrene	252	253	0.213	d ₁₂ -Benzo[a]pyrene	26.36	Benzo[e]pyrene
Benzo[a]pyrene	252	253	0.217	d ₁₂ -Benzo[a]pyrene	26.58	Benzo[a]pyrene
Perylene	252	253	0.212	d ₁₂ -Perylene	27.00	Perylene
Dibenzo[ah]anthracene ²	278	139	0.144	d ₁₄ -Dibenzo[ah]anthracene	31.86	Dibenz[ah]anthracene
Indeno[1,2,3-cd]pyrene	276	138	0.179	d ₁₂ -Indeno[1,2,3,cd]pyrene	31.71	Indeno[1,2,3-cd]pyrene
Benzo[ghi]perylene	276	138	0.194	d ₁₂ -Benzo[ghi]perylene	32.53	Benzo[ghi]perylene
Biphenyl ³	154	152	0.304	d ₁₀ -Biphenyl	9.81	Biphenyl
Dibenzothiophene ³	184	152	0.073	d ₁₀ -Phenanthrene	14.72	Dibenzothiophene
1-Methylnaphthalene ³ 142		141	0.962	d ₁₀ -2-Methylnaphthalene	8.81	1-Methylnaphthalene
2-Methylnaphthalene ³	142	141	0.930	d ₁₀ -2-Methylnaphthalene	8.55	2-Methylnaphthalene
1-Naphthalenes ³	142	⁴	⁴	d ₁₀ -2-Methylnaphthalene	⁵	1- & 2-Methylnaphthalene
2,6-Dimethylnaphthalene ³	156	141	0.666	d ₁₂ -2,6 Dimethylnaphthalene	10.17	2,6-Dimethylnaphthalene
1,2-Dimethylnaphthalene	156	141	1.26	d ₁₂ -2,6 Dimethylnaphthalene	10.90	1,2-Dimethylnaphthalene
C2-Naphthalenes ³	156	⁴	⁴	d ₁₂ -2,6 Dimethylnaphthalene	⁵	2,6- & 1,2-Dimethylnaphthalene
2,3,5-Trimethylnaphthalene ³	170	155	0.873	d ₁₂ -2,6 Dimethylnaphthalene	12.35	2,3,5- Trimethylnaphthalene
2,3,6-Trimethylnaphthalene	170	155	0.876	d ₁₂ -2,6 Dimethylnaphthalene	12.17	2,3,6- Trimethylnaphthalene
C3-Naphthalenes ³	170			d ₁₂ -2,6 Dimethylnaphthalene	⁵	2,3,5- & 2,3,6- Trimethylnaphthalene
1,4,6,7-Tetramethylnaphthalene	184	139	0.027	d ₁₂ -2,6 Dimethylnaphthalene	13.89	1,4,6,7-Tetramethylnaphthalene
C4-Naphthalene		⁴	⁴	d ₁₂ -2,6 Dimethylnaphthalene	⁵	1,4,6,7-Tetramethylnaphthalene
2-Methylantracene	192	191	0.531	d ₁₀ -Phenanthrene	16.45	2-Methylantracene

¹ Coelutes with Triphenylene² Coelutes with Dibenz[ac]anthracene³ These compounds are in addition to the regular suite of analytes, and are analyzed by client request only.⁴ Secondary ion confirmation procedures do not apply⁵ RRT ranges apply to alkylated PAH Totals

AXYS ANALYTICAL SERVICES LTD

TARGET ANALYTES	Quantification Ion (m/z)	Confirmation Ions (m/z)	Typical Ion Ratio (Conf./Quant.)	SURROGATE	Typical Retention Time (minutes)	RRF DETERMINED FROM
3-Methylphenanthrene	192	191	0.608	d ₁₀ -Phenanthrene	16.27	1- & 2-Methylphenanthrene & 2-Methylanthracene
2-Methylphenanthrene	192	191	0.608	d ₁₀ -Phenanthrene	16.36	2-Methylphenanthrene
9/4-Methylphenanthrenes	192	191	0.634	d ₁₀ -Phenanthrene	16.59	1- & 2-Methylphenanthrene & 2-Methylanthracene
1-Methylphenanthrene ³	192	191	0.634	d ₁₀ -Phenanthrene	16.64	1-Methylphenanthrene
C1-Phenanthrenes/Anthracenes ³	192	4	4	d ₁₀ -Phenanthrene	5	1- & 2-Methylphenanthrene & 2-Methylanthracene
3,6-Dimethylphenanthrene ³	206	191	0.342	d ₁₀ -Fluoranthrene	17.46	3,6-Dimethylphenanthrene
2,6-Dimethylphenanthrene	206	191	0.342	d ₁₀ -Fluoranthrene	17.54	3,6- & 1,7-Dimethylphenanthrenes
1,7-Dimethylphenanthrene	206	191	0.332	d ₁₀ -Fluoranthrene	17.89	1,7-Dimethylphenanthrene
1,8-Dimethylphenanthrene	206	191	0.332	d ₁₀ -Fluoranthrene	18.13	3,6- & 1,7-Dimethylphenanthrenes
C2-Phenanthrenes/Anthracenes ³	206	4	4	d ₁₀ -Fluoranthrene	5	3,6- & 1,7-Dimethylphenanthrenes
1,2,6-Trimethylphenanthrene	220	205	0.581	d ₁₀ -Fluoranthrene	19.41	1,2,6-Trimethylphenanthrene
C3-Phenanthrenes/Anthracenes				d ₁₀ -Fluoranthrene	5	1,2,6-Trimethylphenanthrene
Retene ³	234	219	1.63	d ₁₀ -Fluoranthrene	19.53	Retene
C4-Phenanthrenes/Anthracenes	234	4	4	d ₁₀ -Fluoranthrene	5	Retene
C1-Biphenyls	168	4	4	d ₁₀ -Biphenyl	5	Biphenyl
C2-Biphenyls	182	4	4	d ₁₀ -Biphenyl	5	Biphenyl
C1-Acenaphthenes	168	4	4	d ₈ -Acenaphthylene	5	Acenaphthene
2-Methylfluorene	180	165	1.23	d ₁₀ -Phenanthrene	14.06	2-Methylfluorene
C1-Fluorenes	180	4	4	d ₁₀ -Phenanthrene	5	2-Methylfluorene
1,7-Dimethylfluorene	194	177	0.092	d ₁₀ -Phenanthrene	15.49	1,7-Dimethylfluorene
C2-Fluorenes	194	4	4	d ₁₀ -Phenanthrene	5	1,7-Dimethylfluorene
C3-Fluorenes	208	4	4	d ₁₀ -Phenanthrene	5	1,7-Dimethylfluorene
2/3-Methyldibenzothiophenes	198	197	0.738	d ₁₀ -Phenanthrene	16.07	2/3-Methyldibenzothiophenes
C1-Dibenzothiophenes	198	4	4	d ₁₀ -Phenanthrene	5	2/3-Methyldibenzothiophenes
2,4-Dimethyldibenzothiophene	212	197	0.514	d ₁₀ -Phenanthrene	17.08	2,4-Dimethyldibenzothiophene
C2-Dibenzothiophenes	212	4	4	d ₁₀ -Phenanthrene	5	2,4-Dimethyldibenzothiophene
C3-Dibenzothiophenes	226	4	4	d ₁₀ -Phenanthrene	5	2,4-Dimethyldibenzothiophene
C4-Dibenzothiophenes	240	4	4	d ₁₀ -Phenanthrene	5	2,4-Dimethyldibenzothiophene
3-Methylfluoranthene/Benzo(a)fluorene	216	215	0.880	d ₁₀ -Fluoranthrene	19.53	3-Methylfluoranthene
C1-Fluoranthenes/Pyrenes	216	4	4	d ₁₀ -Fluoranthrene	5	3-Methylfluoranthene
C2-Fluoranthenes/Pyrenes	230	4	4	d ₁₀ -Fluoranthrene	5	3-Methylfluoranthene
C3-Fluoranthenes/Pyrenes	244	4	4	d ₁₀ -Fluoranthrene	5	3-Methylfluoranthene
C4-Fluoranthenes/Pyrenes	258	4	4	d ₁₀ -Fluoranthrene	5	3-Methylfluoranthene
5/6-Methylchrysenes	242	4	4	d ₁₂ -Chrysene	23.15	6-Methylchrysene
1-Methylchrysene	242	4	4	d ₁₂ -Chrysene	23.32	1-Methylchrysene
C1-Benz(a)anthracenes/Chrysenes	242	4	4	d ₁₂ -Chrysene	5	1- & 6-Methylchrysenes
5,9-Dimethylchrysene	256	4	4	d ₁₂ -Chrysene	24.49	5,9-Dimethylchrysene

AXYS ANALYTICAL SERVICES LTD

TARGET ANALYTES	Quantification Ion (m/z)	Confirmation Ions (m/z)	Typical Ion Ratio (Conf./Quant.)	SURROGATE	Typical Retention Time (minutes)	RRF DETERMINED FROM
C2-Benz(a)anthracenes/Chrysenes	256	⁴	⁴	d ₁₂ -Chrysene	⁵	5,9-Dimethylchrysene
C3-Benz(a)anthracenes/Chrysenes	270	⁴	⁴	d ₁₂ -Chrysene	⁵	5,9-Dimethylchrysene
C4-Benz(a)anthracenes/Chrysenes	284	⁴	⁴	d ₁₂ -Chrysene	⁵	5,9-Dimethylchrysene
7-Methylbenzo(a)pyrene	266	⁴	⁴	d ₁₂ -Benzo[a]pyrene	29.35	7-Methylbenzo(a)pyrene
C1-Benzofluoranthenes/Benzopyrenes	266	⁴	⁴	d ₁₂ -Benzo[a]pyrene	⁵	7-Methylbenzo(a)pyrene
C2-Benzofluoranthenes/Benzopyrenes	280	⁴	⁴	d ₁₂ -Benzo[a]pyrene	⁵	7-Methylbenzo(a)pyrene
LABELLED SURROGATE STANDARDS	Quantification Ion (m/z)	Confirmation Ions (m/z)		RECOVERY CALCULATED AGAINST		
d ₈ -Naphthalene	136	134	0.095	d ₁₀ -Acenaphthene	6.80	
d ₁₀ -2-Methylnaphthalene	152	151	0.195	d ₁₀ -Acenaphthene	8.47	
d ₁₀ -Biphenyl	164	⁴	⁴	d ₁₀ -Acenaphthene	9.75	
d ₁₂ -2,6-Dimethylnaphthalene	168	150	0.747	d ₁₀ -Acenaphthene	10.07	
d ₈ -Acenaphthylene	160	158	0.159	d ₁₀ -Acenaphthene	10.80	
d ₁₀ -Phenanthrene	188	184	0.143	d ₁₀ -Pyrene	14.97	
d ₁₀ -Fluoranthene	212	208	0.173	d ₁₀ -Pyrene	18.02	
d ₁₂ -Benz[a]anthracene	240	236	0.250	d ₁₀ -Pyrene	21.63	
d ₁₂ -Chrysene	240	236	0.278	d ₁₀ -Pyrene	21.73	
d ₁₂ -Benzo[b]fluoranthene	264	260	0.216	d ₁₂ -Benzo[e]pyrene	25.11	
d ₁₂ -Benzo[k]fluoranthene	264	260	0.208	d ₁₂ -Benzo[e]pyrene	25.23	
d ₁₂ -Benzo[a]pyrene	264	260	0.216	d ₁₂ -Benzo[e]pyrene	26.47	
d ₁₂ -Perylene	264	260	0.256	d ₁₂ -Benzo[e]pyrene	26.88	
d ₁₂ -Indeno[1,2,3,cd]pyrene	288	284	0.192	d ₁₂ -Benzo[e]pyrene	31.63	
d ₁₄ -Dibenzo[ah]anthracene	292	288	0.260	d ₁₂ -Benzo[e]pyrene	31.75	
d ₁₂ -Benzo[ghi]perylene	288	284	0.205	d ₁₂ -Benzo[e]pyrene	32.45	
LABELLED RECOVERY STANDARDS	Quantification Ion (m/z)	Confirmation Ions (m/z)				
d ₁₀ -Acenaphthene	164	160	0.464		11.24	
d ₁₀ -Pyrene	212	208	0.176		18.56	
d ₁₂ -Benzo[e]pyrene	264	260	0.269		26.25	

CALIBRATION

Initial calibration is performed using a five point calibration series of solutions that encompass the working concentration range. Initial calibration solutions contain the suite of labelled surrogate and recovery standards and authentic target PAHs listed as “PAHs and alkylated PAHs determined by multi-point calibration”. Calibration procedures use the mean RRFs determined from the initial calibration to calculate analyte concentrations. Calibration is verified at least once every 12 hours by analysis of a mid-level calibration solution.

An additional calibration solution contains the suite of labelled surrogate and recovery standards and authentic target PAHs listed as “PAHs and alkylated PAHs determined by single-point calibration”. This calibration solution is analyzed at the beginning and end of each batch (bracket) of samples and is used to establish the relative response factors. The mean RRFs determined from the single calibration solution run before and after the samples are used for quantification of sample results.

Concentration of PAHs/Alkylated PAHs Calibration Standard Solutions

TARGET ANALYTE	Level A (Sens. Std) (ng/mL)	Concentration of Calibration Standard Solutions (ng/mL)					Conc. Of Native Std (Low Level) (ng/mL)	Conc. Of Native Std (High Level) (ng/mL)
		Level B	Level C	Level D	Level E	Level F		
Acenaphthene	10	50	100	500	2000	5000	2000	20 000
Acenaphthylene	10	50	100	500	2000	5000	2000	20 000
Anthracene	10	50	100	500	2000	5000	2000	20 000
Benz[a]anthracene	10	50	100	500	2000	5000	2000	20 000
Benzo[b]fluoranthene	10	50	100	500	2000	5000	2000	20 000
Benzo[k]fluoranthene	10	50	100	500	2000	5000	2000	20 000
Benzo[ghi]perylene	10	50	100	500	2000	5000	2000	20 000
Benzo[a]pyrene	10	50	100	500	2000	5000	2000	20 000
Benzo[e]pyrene	10	50	100	500	2000	5000	2000	20 000
Biphenyl	10	50	100	500	2000	5000	2000	20 000
Chrysene	10	50	100	500	2000	5000	2000	20 000
Dibenzo[ah]anthracene	10	50	100	500	2000	5000	2000	20 000
2,6-Dimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
Fluoranthene	10	50	100	500	2000	5000	2000	20 000
Fluorene	10	50	100	500	2000	5000	2000	20 000
Indeno[1,2,3-cd]pyrene	10	50	100	500	2000	5000	2000	20 000
1-Methylnaphthalene	10	50	100	500	2000	5000	2000	20 000
2-Methylnaphthalene	10	50	100	500	2000	5000	2000	20 000
1-Methylphenanthrene	10	50	100	500	2000	5000	2000	20 000
Naphthalene	10	50	100	500	2000	5000	2000	20 000
Perylene	10	50	100	500	2000	5000	2000	20 000
Phenanthrene	10	50	100	500	2000	5000	2000	20 000
Pyrene	10	50	100	500	2000	5000	2000	20 000
2,3,5-Trimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
Dibenzothiophene	10	50	100	500	2000	5000	2000	20 000
3,6-Dimethylphenanthrene	10	50	100	500	2000	5000	2000	20 000
Retene	10	50	100	500	2000	5000	2000	20 000
2-Methylanthracene	10	50	100	500	2000	5000	2000	20 000
1,2-Dimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
2-Methylphenanthrene	10	50	100	500	2000	5000	2000	20 000
1,2,6-Trimethylphenanthrene	10	50	100	500	2000	5000	2000	20 000
2,3,6-Trimethylnaphthalene	10	50	100	500	2000	5000	2000	20 000
1,7-Dimethylphenanthrene	10	50	100	500	2000	5000	2000	20 000
1,4,6,7-Tetramethylnaphthalene	10	50	100	500	2000	5000	2000	20 000

AXYS Analytical Services Ltd.

LABELLED SURROGATE STANDARDS	Level A (Sens. Std) (ng/mL)	Concentration of Calibration Standard Solutions					Conc. Of Surrogate Std (Low Level) (ng/mL)	Conc. Of Surrogate Std (High Level) (ng/mL)
		Level B	Level C	Level D	Level E	Level F		
d ₈ -Naphthalene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₀ -2-Methylnaphthalene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₈ -Acenaphthylene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₀ -Phenanthrene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₀ -Fluoranthene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₂ -Benz[a]anthracene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₂ -Chrysene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₂ -2,6-Dimethylnaphthalene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₂ -Benzo[b]fluoranthene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₂ -Benzo[k]fluoranthene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₂ -Benzo[a]pyrene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₂ -Perylene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₂ -Indeno[1,2,3-cd]pyrene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₄ -Dibenzo[ah]anthracene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₂ -Benzo[ghi]perylene	2000	2000	2000	2000	2000	2000	2000	20 000
d ₁₀ -Biphenyl	2000	2000	2000	2000	2000	2000	2000	20 000
LABELLED RECOVERY STANDARDS							Conc. Of Recovery Std (Low Level) (ng/mL)	Conc. Of Recovery Std (High Level) (ng/mL)
d ₁₀ -Acenaphthene	2000	2000	2000	2000	2000	2000	4000	20 000
d ₁₀ -Pyrene	2000	2000	2000	2000	2000	2000	4000	20 000
d ₁₂ -Benzo[e]pyrene	2000	2000	2000	2000	2000	2000	4000	20 000

Concentrations of PAHs/Alkylated PAHs Single Point Calibration Solution

TARGET ANALYTE	Single Point Calibration Solution (ng/mL)	Conc. Of Native Std (Low Level) (ng/mL)	Conc. Of Native Std (High Level) (ng/mL)
2-Methylfluorene	2000	2000	20 000
1,7-Dimethylfluorene	2000	2000	20 000
2-Methyldibenzothiophene	2000	2000	20 000
2,4-Dimethyldibenzothiophene	2000	2000	20 000
5,9-Dimethylchrysene	2000	2000	20 000
7-Methylbenzo(a)pyrene	2000	2000	20 000
3-Methylfluoranthene	2000	2000	20 000
6-Methylchrysene	2000	2000	20 000
1-Methylchrysene	2000	2000	20 000
LABELLED SURROGATE STANDARDS		Conc. Of Surrogate Std (Low Level) (ng/mL)	Conc. Of Surrogate Std (High Level) (ng/mL)
d ₈ -Naphthalene	2000	2000	20 000
d ₁₀ -2-Methylnaphthalene	2000	2000	20 000
d ₈ -Acenaphthylene	2000	2000	20 000
d ₁₀ -Phenanthrene	2000	2000	20 000
d ₁₀ -Fluoranthene	2000	2000	20 000
d ₁₂ -Benz[a]anthracene	2000	2000	20 000
d ₁₂ -Chrysene	2000	2000	20 000
d ₁₂ -2,6-Dimethylnaphthalene	2000	2000	20 000
d ₁₂ -Benzo[b]fluoranthene	2000	2000	20 000
d ₁₂ -Benzo[k]fluoranthene	2000	2000	20 000
d ₁₂ -Benzo[a]pyrene	2000	2000	20 000

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d ₁₂ -Perylene	2000	2000	20 000
d ₁₂ -Indeno[1,2,3-cd]pyrene	2000	2000	20 000
d ₁₄ -Dibenzo[ah]anthracene	2000	2000	20 000
d ₁₂ -Benzo[ghi]perylene	2000	2000	20 000
d ₁₀ -Biphenyl	2000	2000	20 000
LABELLED RECOVERY STANDARDS		Conc. Of Surrogate Std (Low Level) (ng/mL)	Conc. Of Surrogate Std (High Level) (ng/mL)
d ₁₀ -Acenaphthene	2000	4000	20 000
d ₁₀ -Pyrene	2000	4000	20 000
d ₁₂ -Benzo[e]pyrene	2000	4000	20 000

ANALYTE IDENTIFICATION

A chromatographic peak is identified as a target compound if the following criteria are met for the quantification and confirmation ions (where confirmation ions are available):

1. Peak responses must be at least three times the background noise level.
2. The retention time must be within three seconds of that predicted from the calibration run and the sample retention time reference (labelled compound).
3. Peak centroids for the quantification and confirmation ions must coincide within two seconds.
4. The relative ion abundance ratios must be within 20% of the opening calibration values.

QUANTIFICATION

Concentrations of target PAHs are calculated using the isotope dilution method of quantification. Compounds are quantified by comparing the area of the quantification ion to that of the corresponding deuterium-labelled standard and correcting for response factors. Response factors are determined daily using authentic PAHs. Calculations are carried out using HP EnviroQuant and Prolab MS-Extended for targeting and quantification.

$$\text{Concentration of Target (ng/g or ng/L)} = \left(\frac{\text{area of Target}}{\text{area of Surr Std}} \right) \times \left(\frac{\text{weight of Surr Std (ng)}}{\text{RRF}} \right) \times \left(\frac{1}{\text{weight of sample (g or L)}} \right)$$

$$\text{where RRF} = \left(\frac{\text{area of Target}}{\text{area of Surr Std}} \right) \times \left(\frac{\text{concentration of Surr Std}}{\text{concentration of Target}} \right)$$

and the Surr Std is either the surrogate or the internal standard

REPORTING LIMITS

Concentrations and detection limits for the target PAHs are reported. Typical reporting units for all data are ng/g, ng/L, or ng/sample. Concentrations for solids are reported on a dry weight basis. Concentrations in tissues (including blood and milk) are reported on a wet weight basis and/or on a lipid weight basis when requested. Concentrations in aqueous are reported on a volume basis. Concentrations in XAD-2 resin, filters and stack gas samples are reported on a per sample basis or a per volume basis. Concentrations in particulate filters are reported on a per sample basis.

The following are commonly requested reporting limits:

Sample Specific Detection Limit or Sample Detection Limit (SDL) – determined individually for every sample analysis run by converting the area equivalent of 3.0 times (2.5 times for EPA 1600 series methods) the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. The SDL accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up. Equivalent term(s): Estimated Detection Limit (EDL) from EPA method 8290.

Method Detection Limit (MDL) - determined as specified by EPA Fed. Reg. 40 CFR Part 136 Appendix B (no iteration option). The 99% confidence level MDL is determined based on analysis of a minimum of 7 replicate matrix spikes fortified at 1-10 times the estimated detection limit. MDL is determined as required based on accreditation, contract and workload requirements.

Lower Method Calibration Limit (LMCL) - determined by prorating the concentration of the lowest calibration limit for sample size and extract volume. The following equation is used. $((\text{lowest level cal conc.}) \times (\text{extract volume})) / \text{sample size}$. Typical extract volume for aqueous and tissue samples is 100 µL for all other matrices typical extract volume is 500 µL.

For the analysis of PAHs AXYS standard is to report sample concentrations using the SDL as the reporting limit.

QUALITY ASSURANCE/QUALITY CONTROL

All samples are analyzed in batches with the following composition:

- Batch Size - Each batch consists of up to twenty test samples and additional QC samples.
- Blanks - One procedural blank is analyzed for each batch. The procedural blank is prepared by spiking an aliquot of the surrogate standard solution into a clean matrix.
- On-going Precision and Recovery (OPR) Samples – On-going Precision and Recovery (OPR) is demonstrated by the analysis of a spiked reference matrix (SPM) analyzed with each batch. The reference sample to be analyzed is assigned to the analyst when the batch is assigned. The OPR sample is prepared by spiking an aliquot of the authentic spiking solution into an accurately weighed in-house reference matrix (known to contain low background levels of target analytes). The matrix is spiked with an aliquot of surrogate standard solution and, after an equilibration time of at least 30 minutes is extracted.
- Duplicates - Sample duplicates are analyzed (provided sufficient sample is available) for batches with 7-20 test samples, or when specified by the contract. For some matrices (XAD columns, filters, air samples) only field duplicates (if available) can be analyzed.
- Reference Samples – Certified reference materials are commercially available and are used to validate and periodically check methods. Additionally reference samples may be analyzed with a batch at the client's request.

The batch composition may vary according to batch or quality control requirements specified by a client. Each batch is carried through the complete analytical process as a unit. For sample data to be reportable the batch QC data must meet the acceptance criteria.

QC Specification Table: Authentic and Surrogate Standard Recoveries, OPR and Samples

MATRIX	Typical Sample Specific* Detection Limits						Procedural Blank Level (ng)	Acceptable Matrix Spike % Recovery
	Solid	Aqueous	Tissue	XAD-2 Column	PUF	Filter		
Analyte:	ng/g	ng/L	ng/g	ng	ng	ng		
Naphthalene	0.5	5	0.1	5	5	5	<10	70-130
Acenaphthylene	0.5	5	0.1	5	5	5	<5	70-140
Acenaphthene	0.5	5	0.1	5	5	5	<5	70-130
Fluorene	0.5	5	0.1	5	5	5	<5	60-140
Phenanthrene	0.5	5	0.1	5	5	5	<10	70-130
Anthracene	0.5	5	0.1	5	5	5	<5	70-130
Fluoranthene	0.5	5	0.1	5	5	5	<5	70-130
Pyrene	0.5	5	0.1	5	5	5	<5	70-130
Benz(a)anthracene	0.5	5	0.1	5	5	5	<5	70-130
Chrysene	0.5	5	0.1	5	5	5	<5	70-130
Benzo(b)fluoranthene	0.5	5	0.1	5	5	5	<5	70-130
Benzo(j/k)fluoranthenes	0.5	5	0.1	5	5	5	<5	70-130
Benzo(e)pyrene	0.5	5	0.1	5	5	5	<5	70-130
Benzo(a)pyrene	0.5	5	0.1	5	5	5	<5	70-130
Perylene	1.0	10	0.2	10	10	10	<5	70-130
Dibenzo(ah)anthracene	1.0	10	0.2	10	10	10	<5	70-130
Indeno(1,2,3-cd)pyrene	1.0	10	0.2	10	10	10	<5	70-130
Benzo(ghi)perylene	1.0	10	0.2	10	10	10	<5	70-130
Biphenyl	1.0	10	0.2	10	10	10	<5	70-130
Dibenzothiophene	1.0	10	0.2	10	10	10	<5	60-140
1-Methylnaphthalene	1.0	10	0.2	10	10	10	<5	70-130
2-Methylnaphthalene	1.0	10	0.2	10	10	10	<5	70-130
2,6-Dimethylnaphthalene	1.0	10	0.2	10	10	10	<10	70-130
1,2-Dimethylnaphthalene	1.0	10	0.2	10	10	10	<10	60-140
2,3,5-Trimethylnaphthalene	1.0	10	0.2	10	10	10	<10	50-150
2,3,6-Trimethylnaphthalene	1.0	10	0.2	10	10	10	<10	50-150
1,4,6,7-Tetramethylnaphthalene	1.0	10	0.2	10	10	10	<10	50-200
2-Methylantracene	1.0	10	0.2	10	10	10	<5	50-150
3-Methylphenanthrene	1.0	10	0.2	10	10	10	<10	N.A.
2-Methylphenanthrene	1.0	10	0.2	10	10	10	<10	50-150
9/4-Methylphenanthrenes	1.0	10	0.2	10	10	10	<10	N.A.
1-Methylphenanthrene	1.0	10	0.2	10	10	10	<10	50-150
3,6-Dimethylphenanthrene	1.0	10	0.2	10	10	10	<10	50-150
2,6-Dimethylphenanthrene	1.0	10	0.2	10	10	10	<10	N.A.
1,7-Dimethylphenanthrenes	1.0	10	0.2	10	10	10	<10	50-150
1,8-Dimethylphenanthrene	1.0	10	0.2	10	10	10	<10	N.A.
1,2,6-Trimethylphenanthrene	1.0	10	0.2	10	10	10	<10	50-150
Retene	1.0	10	0.2	10	10	10	<5	50-150
2-Methylfluorene	1.0	10	0.2	10	10	10	<5	50-150
1,7-Dimethylfluorene	1.0	10	0.2	10	10	10	<5	50-150
2/3-Methyldibenzo-thiophenes	1.0	10	0.2	10	10	10	<10	50-150
2,4-Dimethyldibenzothiophene	1.0	10	0.2	10	10	10	<5	50-150
3-Methylfluoranthene/ Benzo(a)fluorene	1.0	10	0.2	10	10	10	<5	50-150

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5/6-Methylchrysenes	1.0	10	0.2	10	10	10	<5	50-150
1-Methylchrysene	1.0	10	0.2	10	10	10	<5	50-150
5,9-Dimethylchrysene	1.0	10	0.2	10	10	10	<5	50-150
7-Methylbenzo(a)pyrene	1.0	10	0.2	10	10	10	<5	50-150
Typical Sample Size	10 g	1 L	10 g	1 col	1 PUF	1 filter		
Typical Final Volume (µL)	500	100	100	500	500	500		

*Detection limits quoted are those routinely achieved. Lower detection limits can be achieved if required.

NOTE: QC acceptance criteria do not apply to alkylated PAH total values (e.g. C1-phenanthrenes/anthracenes) as these are Tentatively Identified Compounds (TIC) of unknown accuracy.

SURROGATE STANDARD

RECOVERIES:

d₈-naphthalene 15
 d₈-acenaphthylene 20
 d₁₀-phenanthrene 30
 d₁₀-fluoranthene 30
 d₁₂-benz[a]anthracene 30
 d₁₂-chrysene 30
 d₁₂-benzo[b]fluoranthene
 d₁₂-benzo[k]fluoranthene
 d₁₂-benzo[a]pyrene 30
 d₁₂-perylene 30
 d₁₄-dibenz[ah]anthracene 30
 d₁₂-indeno[1,2,3-cd]pyrene 30
 d₁₂-benzo[ghi]perylene 30
 d₁₀-2-methylnaphthalene 20
 d₁₂-2,6-dimethylnaphthalene 20
 d₁₀-biphenyl

% RECOVERY RANGES

ALL MATRICES

– 130
 – 130
 – 130
 – 130
 – 130
 – 130
 30 – 130
 30 – 130
 – 130
 – 130
 – 130
 – 130
 – 130
 – 130
 15 – 130

QC Specification Table: Instrumental Analysis, and Analyte Quantification

Parameter	Acceptance Specification
Procedural Blank	Refer to Table "QC Specification Table: Authentic and Surrogate Standard Recoveries, OPR and Samples" above, or 5 times lower than analogous analyte value detected in the samples.
Analysis Duplicate	Duplicates must fall within $\pm 20\%$ of the mean (applicable to concentrations > 10 times the DL) These are guidelines – departures based on professional judgement allowed.
Instrument Sensitivity	S/N 3:1 for 10 pg of acenaphthene, dibenzo(a,h)anthracene.
Instrument Resolution	Calibration gas PFTBA (FC43) unit mass resolution at m/e 69/70 and 219/220, Unit mass resolution is demonstrated by the presence of a resolved peak at m/z 70 and m/e 220.
Instrument Linearity	Linearity is demonstrated by a 5-point calibration over the working concentration range with a relative standard deviation of the RRFs $\leq 20\%$ for targets with a labelled analog present and all labelled compounds, $\leq 35\%$ for targets with no labelled analog present.
Bracketing Cal	RRFs for the opening and closing calibrations over a 12 hour period must agree to within $\pm 20\%$ of the mean (ie < 40 RPD between RRFs and for the opening and closing calibrations).
Continuing Cal Ver	Opening Cal Ver: Concentrations of native compounds and labelled surrogates must be within $\pm 25\%$ of expected values for all targets. Closing Cal Ver: Concentrations of native compounds must be within $\pm 25\%$ of expected values. Concentrations of labelled surrogates must be within $\pm 25\%$ of expected values, with any two (2) values allowed to be within $\pm 40\%$
GC Resolution	Benzo[b] & [k]fluoranthene valley height must be $\leq 75\%$ for equal concentrations. Phenanthrene/anthracene valley height must be $\leq 30\%$ for equal concentrations.
Chromatogram Quality	Maximum peak width must be ≤ 15 seconds for dibenzo[ghi]perylene peak at 10% peak height.
Retention Time Window for Target Compounds	RT within ± 3 seconds of the predicted retention time determined from the calibration standard and adjusted relative to the peak retention time reference (i.e. labelled surrogate). A second requirement is that an authentic elute after its labelled analog.
Ion Abundance Ratios	CAL VER: Ion ratios for dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within $\pm 35\%$ of the mid-point of the I-CAL. All other native analytes and labelled surrogates must be $\pm 20\%$ of the mid-point of the I-CAL. Samples: Ion ratios for dibenz[ah]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene must be within $\pm 35\%$ of the 12 hour CAL (CAL VER or Bracketing) calibration standard. All other native analytes and labelled surrogates must be $\pm 20\%$ of the 12 hour CAL (CAL VER or Bracketing) calibration standard.

APPENDIX – SUMMARY OF MODIFICATIONS TO EPA 8270C, 8270D AND 1625B

Analysis by GC/LRMS, Key Attributes of AXYS MLA-021, EPA 8270C/D and EPA 1625B				
	MLA-021	EPA 8270C	EPA 8270D	EPA 1625B
MS acquisition mode	SIM ¹	Full Scan or optional SIM ¹	Full Scan or optional SIM ¹	Full Scan
Qualitative Identification Criteria	Retention time & ratio of 2 ions	Retention time & ratio of 3 ² ions	Retention time & ratio of 3 ² ions	Retention time & ratio of all characteristic ions
MS Ion Ratio Criteria	Within 20 % of theoretical	Within 30 % of reference spectrum	Within 30 % of reference spectrum	Within -50 % and +200 % of reference spectrum
MS Tuning Type and Check Frequency	PTFBA, daily	DFTTP ³ , 12 hrs	DFTTP ³ , 12 hrs	DFTTP, 8 hrs
Quantification References	Isotopically labeled standards added prior to extraction	Internal standards added just before instrumental analysis	Internal standards added just before instrumental analysis	Isotopically labeled standards added prior to extraction
Recovery correction of results	YES	NO	NO	YES
Calibration, minimum # levels	CCV Procedure: 5 levels OPTIONAL Single Point BRACKETING: 1 level	5	5	5
Initial Calibration Limit (% rsd)	20 % (35 % for targets with no labelled analog)	15 %	20 %	20 % (35 % for targets with no labelled analog)
Calibration Verification Frequency	Initially and every 12 hrs	Initially and every 12 hrs	Initially and every 12 hrs	Initially and every 8 hrs
Calibration Verification Relative Response Limit (% diff.)	< 25 % of I-CAL	< 20 % of I-CAL	< 20 % of I-CAL	Vary by compound; most stringent is acenaphthene: -20% to +25% of I-CAL
Calibration Verification IS area (% of I-CAL midpoint)	50-200 %	50-200 %	50-200 %	n.a.
Calibration verification IS RT (diff. from I-CAL midpoint)	n.a.	30 sec.	30 sec.	n.a.

Notes:

¹ SIM (Selected Ion Monitoring) is an allowable alternate technique for high sensitivity applications

² Based on availability, use of less ions is permitted where necessary

³ Alternate MS tuning protocols are permitted

Appendix N
Laboratory SOPs

AXYS SOP
MLA-035, Revision 6 Summary

Chlorinated Pesticides
By EPA 1613B

Summary of AXYS Method MLA-035 Rev 06:

Analytical Method for the Analysis of Multi-Residue Pesticides by HRGC/HRMS

This document describes the analytical method for the determination of selected organochlorine, organophosphorous, organonitrogen and triazine pesticides from aqueous, soil, sediment, sludge, tissue, XAD-2 resin and filter samples.

Target Analytes

Organochlorine (OCP) Analytes	Organophosphate (OPP) Analytes
Aldrin	Azinphos-Methyl
Chlordane, alpha (cis)	Chlorpyrifos
Nonachlor, cis-	Chlorpyrifos-Methyl
Heptachlor	Chlorpyrifos-Oxon
Oxychlordane	Diazinon
Chlordane, gamma (trans)	Diazinon-Oxon
Nonachlor, trans-	Dimethoate
HCH, alpha	Disulfoton Sulfone
HCH, beta	Disulfoton
HCH, gamma	Ethion
HCH, delta	Fenitrothion
alpha-Endosulphan	Fonofos
beta-Endosulphan	Malathion
Dieldrin	Methamidophos
Endosulphan-Sulphate	Parathion-Ethyl
Endrin	Parathion-Methyl
Endrin-Ketone	Phorate
Heptachlor-Epoxide	Phosmet
Methoxychlor	Pirimiphos-Methyl
Captan	Terbufos
Chlorothalonil	
Dacthal	Triazine Pesticides
Hexachlorobenzene	Ametryn
Mirex	Atrazine
Octachlorostyrene	Cyanazine
Quintozone	Desethylatrazine
Tecnazene	Hexazinone
o,p-DDE	Metribuzin
p,p-DDE	Simazine
o,p-DDD	
p,p-DDD	Pyrethroid Analytes
o,p-DDT	Permethrins
p,p-DDT	Cypermethrins
Perthane	

Organonitrogen (ON) Analytes	
Alachlor	
Butralin	
Butylate	
Dimethenamid	
Ethalfuralin	
Flufenacet	
Flutriafol	
Linuron	
Methoprene	
Metolachlor	
Pendimethalin	
Tebuconazol	
Triallate	
Trifluralin	

EXTRACTION

All samples are spiked with labelled surrogate standards prior to extraction and extracted as per the table below.

Matrix	Extraction
Aqueous	Liquid-liquid extraction with dichloromethane. (Optional “clean water” extraction – 1/20 the amount of labelled standards and 20 µL final volume.)
Solid (sediment, soil, sludge, pulp, ash)	Soxhlet extraction with dichloromethane
Tissue	Soxhlet extraction with dichloromethane
XAD-2 column and filter	XAD-2 adsorbent is drained and Soxhlet extracted with dichloromethane. The aqueous and organic phases of the resulting extract are separated. The aqueous phase is liquid-liquid extracted with dichloromethane and the extracts are combined.

COLUMN CHROMATOGRAPHY CLEANUP

Extracts are routinely cleaned up using the following chromatography columns and procedures:

- Automated Gel Permeation Chromatography (GPC): Solid and tissue samples.
- Aminopropyl SPE column: All samples.
- Microsilica Column: All samples.

INSTRUMENTAL ANALYSIS

Instrumental analysis is performed on a DB-17 MS capillary chromatography column coupled to a high-resolution mass spectrometer (HRMS). The HRMS is operated at a static (8 000) mass resolution (10% valley) in the electron ionization (EI) positive ion mode using multiple ion detection (MID) acquiring two characteristic ions, where available, for each target analyte and surrogate standard. Selected PFK ions are used as a reference for mass lock.

Analyses are acquired in two separate instrumental runs; one in instrumental run for MR compounds (OCP, OPP, pyrethroids and triazines), and a second instrumental run for ON pesticides.

Analyses, Ions, and Quantification References (MR Compounds)

Analyte Name	Quantified against	Typical Retention Time	mass1	mass2	m1/m2 ratio	Ion Ratio Tolerance	(-%)
Methamidophos	¹³ C-PCB-52	8:55	93.9642	94.9721	N/A	35%	35%
Tecnazene	¹³ C-HCB	14:38	258.8761	260.8732	0.78	35%	35%
Phorate	¹³ C-PCB-52	16:05	260.0128	262.0086	6.92	35%	35%
HCB	¹³ C-HCB	15:49	283.8102	285.8072	1.25	25%	25%
alpha-HCH	¹³ C-gamma-HCH	16:29	218.9116	220.9086	2.08	25%	25%
Desethylatrazine	¹³ C-Atrazine	16:47	172.039	174.036	3.11	35%	35%
Terbufos	¹³ C-PCB-52	17:04	232.9696		N/A	N/A	N/A
Quintozene	¹³ C-HCB	17:32	236.8413	238.8384	1.56	35%	35%
Diazinon-Oxon	d ¹⁰ -Diazinon	17:46	273.1004	288.1239	N/A	35%	35%
Diazinon	d ¹⁰ -Diazinon	17:36	276.0698	304.1011	N/A	35%	35%
Simazine	¹³ C-Atrazine	18:15	201.0781	203.0752	3.1	35%	35%
Atrazine	¹³ C-Atrazine	17:54	215.0938	217.0908	3.08	35%	35%
gamma-HCH	¹³ C-gamma-HCH	18:09	218.9116	220.9086	2.08	25%	25%
Disulfoton	¹³ C-PCB-52	18:26	274.0285	275.0318	N/A	35%	35%
Fonotos	¹³ C-Fonotos	18:18	246.0302	247.0336	N/A	35%	35%
Dimethoate	¹³ C-PCB-52	19:24	228.9996		N/A	N/A	N/A
Heptachlor	¹³ C-Heptachlor	19:30	271.8102	273.8072	1.25	25%	25%
beta-HCH	¹³ C-beta-HCH	19:22	218.9116	220.9086	2.08	25%	25%
delta-HCH	¹³ C-delta-HCH	20:55	218.9116	220.9086	2.08	25%	25%
Chlorothalonil	¹³ C-PCB-52	21:00	263.8816	265.8786	0.78	35%	35%
Chlorpyrifos-Methyl	¹³ C-PCB-52	21:17	285.9261	287.9232	1.44	35%	35%
Aldrin	¹³ C-Aldrin	21:08	262.8569	264.854	1.56	25%	25%
Parathion-Methyl	¹³ C-PCB-52	22:19	263.0017	264.0051	N/A	35%	35%
Ametyrn	¹³ C-PCB-52	22:31	227.1205	228.1238	N/A	35%	35%
Pyrimphos-Methyl	¹³ C-PCB-52	22:32	276.0572	290.0728	N/A	35%	35%
Metibuzin	¹³ C-PCB-52	22:56	198.0701	199.0735	N/A	35%	35%
Dacthal	¹³ C-PCB-52	23:08	298.8836	300.8807	0.78	35%	35%
Octachlorostyrene	¹³ C-Aldrin	23:07	270.8443	272.8413	0.63	25%	25%
Chlorpyrifos	¹³ C-PCB-52	23:23	313.9574	315.9545	1.44	35%	35%
Fenitrothion	¹³ C-PCB-52	23:57	260.0146	277.0174	N/A	35%	35%
Malathion	¹³ C-PCB-52	24:01:00	283.9942	285.002	N/A	35%	35%
Oxychloridane	¹³ C-Oxychloridane	24:01:00	262.8569	264.854	1.56	25%	25%
Parathion-Ethyl	¹³ C-PCB-52	24:16:00	291.033	292.0364	N/A	35%	35%
Chlorpyrifos-Oxon	¹³ C-PCB-52	24:18:00	269.949	271.9462	1.54	35%	35%
Heptachlor-Epoxyde	¹³ C ¹² -Heptachlor-Epoxyde	25:04:00	262.8569	264.854	1.56	25%	25%
t-Chloridane	¹³ C-t-Chloridane	26:31:00	262.8569	264.854	1.56	25%	25%
t-Nonachlor	¹³ C-t-Nonachlor	26:40:00	262.8569	264.854	1.56	25%	25%
c-Chloridane	¹³ C-t-Chloridane	27:32:00	262.8569	264.854	1.56	25%	25%
Alpha-Endosulphan	¹³ C ⁹ -alpha-Endosulphan	27:41:00	262.8569	264.854	1.56	25%	25%
Dieldrin	¹³ C-Dieldrin	30:22:00	262.8569	264.854	1.56	25%	25%

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Cyanazine	¹³ C-PCB-52	28:04:00	240.089	242.0861	3.06	35%
o,p-DDE	¹³ C-p,p-DDE	27:55:00	246.0003	247.9974	1.56	25%
p,p-DDE	¹³ C-p,p-DDE	30:27:00	246.0003	247.9974	1.56	25%
Caplan	¹³ C-PCB-52	31:15:00	263.9653	265.9623	1.44	35%
Disulfoton-Sulfone.	¹³ C-PCB-52	32:40:00	213.0173	214.0251	N/A	35%
o,p-DDD	¹³ C-o,p-DDT	32:12:00	235.0081	237.0052	1.56	25%
Perthane	¹³ C-PCB-52	32:52:00	223.1437	224.152	N/A	35%
Endrin	¹³ C ₁₂ -Endrin	32:46:00	262.8569	264.854	1.56	25%
c-Nonachlor	¹³ C-c-Nonachlor	33:11:00	262.8569	264.854	1.56	25%
Ethion	¹³ C-PCB-52	34:39:00	232.9695		N/A	N/A
beta-Endosulphan	¹³ C ₉ -beta-Endosulphan	34:25:00	264.854	262.8569	0.64	25%
Endosulphan-Sulphate	¹³ C ₉ -beta-Endosulphan	36:48:00	264.854	262.8569	0.64	25%
o,p-DDT	¹³ C-o,p-DDT	33:51:00	235.0081	237.0052	1.56	25%
p,p-DDD	¹³ C-p,p-DDT	34:24:00	235.0081	237.0052	1.56	25%
p,p-DDT	¹³ C-p,p-DDT	35:46:00	235.0081	237.0052	1.56	25%
Mirex	¹³ C-Mirex	36:23:00	236.8413	238.8384	1.56	25%
Hexazinone	¹³ C-PCB-52	39:31:00	171.0882	172.0916	N/A	35%
Methoxychlor	¹³ C ₁₂ -Methoxychlor	39:38:00	227.1072	228.1106	N/A	35%
Endrin-Ketone	¹³ C ₁₂ -Endrin	39:40:00	247.8521	249.8491	0.63	25%
Phosmet	¹³ C-PCB-52	40:49:00	160.0399	161.0432	N/A	35%
Azinphos-Methyl	d ₆ -Azinphos-Methyl	42:32:00	160.0511	161.0544	N/A	35%
Permethrins-Peak_1	¹³ C-Permethrins-Peak_1	41:58:00	183.081	184.0843	N/A	35%
Permethrins-Peak_2	¹³ C-Permethrins-Peak_2	42:16:00	183.081	184.0843	N/A	35%
Cypermethrins-Peak_1	¹³ C-Permethrins-Peak_1+2	43:46:00	163.0061	165.0052	1.56	35%
Cypermethrins-Peak_2	¹³ C-Permethrins-Peak_1+2	43:59:00	163.0081	165.0052	1.56	35%
Cypermethrins-Peak_3	¹³ C-Permethrins-Peak_1+2	44:06:00	163.0081	165.0052	1.56	35%
Surrogate Standards						
¹³ C-HCB	¹³ C-PCB-52	15:48	289.8303	291.8273	1.25	25%
d ₁₀ -Diazinon	¹³ C-PCB-52	17:25	282.1074	314.1638	N/A	35%
¹³ C-Atrazine	¹³ C-PCB-52	17:54	218.1038	220.1009	3.08	35%
¹³ C-gamma-HCH	¹³ C-PCB-52	18:08	222.9346	224.9317	0.77	25%
¹³ C-Fonofos	¹³ C-PCB-52	18:17	252.0503	253.0537	N/A	35%
¹³ C-Hepachlor	¹³ C-PCB-52	19:28	276.8269	278.824	1.24	25%
¹³ C-beta-HCH	¹³ C-PCB-52	19:21	222.9346	224.9317	0.77	25%
¹³ C-delta-HCH	¹³ C-PCB-52	20:53	222.9346	224.9317	0.77	25%
¹³ C-Aldrin	¹³ C-PCB-52	21:05	269.8804	271.8775	1.56	25%
¹³ C-Oxychloridane	¹³ C-PCB-52	23:59	269.8804	271.8775	1.56	25%
¹³ C ₁₂ -Heptachlor-Epoxide	¹³ C-PCB-52	25:01:00	269.8804	271.8775	1.56	25%
¹³ C-t-Chlordane	¹³ C-PCB-52	26:29:00	269.8804	271.8775	1.56	25%
¹³ C-t-Nonachlor	¹³ C-PCB-52	26:38:00	269.8804	271.8775	1.56	25%
¹³ C ₉ -alpha-Endosulphan	¹³ C-PCB-52	27:39:00	269.8804	271.8775	1.56	25%
¹³ C-Dieldrin	¹³ C-PCB-52	30:19:00	269.8804	271.8775	1.56	25%
¹³ C-p,p-DDE	¹³ C-PCB-52	30:25:00	258.0406	260.0376	1.56	25%
¹³ C ₁₂ -Endrin	¹³ C-PCB-52	32:43:00	269.8804	271.8775	1.56	25%
¹³ C-c-Nonachlor	¹³ C-PCB-52	33:09:00	269.8804	271.8775	1.56	25%
¹³ C ₉ -beta-Endosulphan	¹³ C-PCB-52	34:23:00	269.8804	271.8775	1.56	25%
¹³ C-o,p-DDT	¹³ C-PCB-52	33:49:00	247.0484	249.0454	1.56	25%
¹³ C-p,p-DDT	¹³ C-PCB-52	35:46:00	247.0484	249.0454	1.56	25%
¹³ C-Mirex	¹³ C-PCB-52	39:22:00	241.8581	243.8551	1.56	25%
¹³ C ₁₂ -Methoxychlor	¹³ C-PCB-52	39:37:00	239.1475	240.1508	N/A	35%

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d ₆ -Azinphos-Methyl	¹³ C-PCB-52	42:27:00	160.0511	161.0544	N/A	35%
¹³ C-Permethrins-Peak_1	¹³ C-PCB-52	41:58:00	189.1011	190.1045	N/A	35%
¹³ C-Permethrins-Peak_2	¹³ C-PCB-52	42:16:00	189.1011	190.1045	N/A	35%
Recovery Standard						
¹³ C-PCB-52			301.9626	303.9597	0.78	25%

NOTE: Permethrins-Peak_1 is the cis isomer and Permethrins-Peak_2 is the trans isomer

Analytes, Ions, and Quantification References (ON Compounds)

Analyte Name	Quantified against labelled standard	Typical Retention Time	mass1	mass2	m1/m2 ratio	Ion Ratio Tolerance
						(+/- %)
Butylate	¹³ C-PCB-52	6:57	156.1388	174.0953	N/A	35%
Ethalfuralin	¹³ C-PCB-52	11:43	316.0909	276.0596	N/A	35%
Trifluralin	¹³ C-PCB-52	11:51	264.0232	306.0702	N/A	35%
Triallate	¹³ C-PCB-52	16:06	268.033	270.03	1.44	35%
Dimethenamid	¹³ C-PCB-52	17:23	230.0406	232.0377	2.68	35%
Alachlor	¹³ C-Alachlor	17:34	160.1126	188.1074	N/A	35%
Methoprene	¹³ C-PCB-52	17:56	191.18	192.1833	N/A	35%
Butralin	¹³ C-PCB-52	18:08	266.1141	267.1174	N/A	35%
Metolachlor	¹³ C-Metolachlor	18:16	162.1283	163.1316	N/A	35%
Flufenacet	¹³ C-PCB-52	18:18	151.0797	210.9789	N/A	35%
Linuron	d ₆ -Linuron	18:28	159.9721	161.9692	1.56	35%
Pendimethalin	¹³ C-PCB-52	19:02	252.0984	253.1018	N/A	35%
Flutrialfol	¹³ C-PCB-52	20:42	219.0621	220.0655	N/A	35%
Tebuconazol	¹³ C-PCB-52	22:09	250.0747	252.0718	3.02	35%
Surrogate Standards						35%
¹³ C-Alachlor	¹³ C-PCB-52	17:34	166.1328	194.1277	N/A	35%
¹³ C-Metolachlor	¹³ C-PCB-52	18:16	168.1484	169.1518	N/A	35%
d ₆ -Linuron	¹³ C-PCB-52	18:24	159.9721	161.9692	1.56	35%
Recovery Standard						
¹³ C-PCB-52		17:57	232.0249	234.022	1.56	25%

CALIBRATION

Initial calibration is performed using a minimum of 5 calibration solutions that encompass the working range of the instrument. The initial calibration is used to determine response factors for target analytes and labelled standards. The calibration is verified at least once every 12 hours by analysis of a mid-level calibration solution (CAL/VER). The mean relative response factors, determined from the initial calibration, or from the mid level calibration run at the beginning and end of the analysis run, are used for the quantification of target analytes.

Concentration of Calibration Standard Solutions (MR Compounds)

	Concentration (ng/mL)						Authentic Standard Amount Added to sample (ng)
	Level AA ¹	Level A	Level B	Level C	Level D	Level E	
Native Compound							
Methamidophos	4	10	30	80	200	400	80
Tecnazene	2	5	15	40	100	200	40
Phorate	4	10	30	80	200	400	80
Hexachlorobenzene	1.6	4	12	32	80	160	32
HCH, alpha	3.2	8	24	64	160	320	64
Desethylatrazine	2	5	15	40	100	200	40
Terbufos	1	2.5	7.5	20	50	100	20
Quintozene	4	10	30	80	200	400	80
Diazinon-Oxon	4	10	30	80	200	400	80
Diazinon	4	10	30	80	200	400	80
Simazine	4	10	30	80	200	400	80
Atrazine	4	10	30	80	200	400	80
HCH, gamma	3.2	8	24	64	160	320	64
Disulfoton	20	50	150	400	1000	2000	400
Fonofos (Dyfonate)	4	10	30	80	200	400	80
Dimethoate	20	50	150	400	1000	2000	400
Heptachlor	1.6	4	12	32	80	160	32
HCH, beta	3.2	8	24	64	160	320	64
HCH, delta	3.2	8	24	64	160	320	64
Chlorothalonil	2	5	15	40	100	200	40
Chlorpyrifos-Methyl	5	12.5	37.5	100	250	500	100
Aldrin	3.2	8	24	64	160	320	64
Parathion-Methyl	12	30	90	240	600	1200	240
Ametryn	4	10	30	80	200	400	80
Pirimphos-Methyl	4	10	30	80	200	400	80
Metribuzin	1	2.5	7.5	20	50	100	20
Dacthal	1	2.5	7.5	20	50	100	20
Octachlorostyrene	1.6	4	12	32	80	160	32
Chlorpyrifos (Dursban)	4	10	30	80	200	400	80
Fenitrothion	4	10	30	80	200	400	80
Malathion	52	130	390	1040	2600	5200	1040
Oxychlorane	3.2	8	24	64	160	320	64
Parathion-Ethyl (Parathion)	4	10	30	80	200	400	80
Chlorpyrifos-Oxon	4	10	30	80	200	400	80
Heptachlor Epoxide	1.6	4	12	32	80	160	32
Chlordane, gamma (trans)	1.6	4	12	32	80	160	32
Nonachlor, trans-	1.6	4	12	32	80	160	32
Chlordane, alpha (cis)	1.6	4	12	32	80	160	32
alpha-Endosulphan	1.6	4	12	32	80	160	32
Dieldrin	1.6	4	12	32	80	160	32
Cyanazine	4	10	30	80	200	400	80
2,4'-DDE	1.6	4	12	32	80	160	32
4,4'-DDE	1.6	4	12	32	80	160	32
Captan	10	25	75	200	500	1000	200
Disulfoton Sulfone	0.32	0.8	2.4	6.4	16	32	6.4
2,4'-DDD	1.6	4	12	32	80	160	32
Perthane	1.6	4	12	32	80	160	32

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Endrin	1.6	4	12	32	80	160	32
Nonachlor, cis-	1.6	4	12	32	80	160	32
Ethion	0.8	2	6	16	40	80	16
beta-Endosulphan	1.6	4	12	32	80	160	32
Endosulphan Sulphate	1.6	4	12	32	80	160	32
2,4'-DDT	1.6	4	12	32	80	160	32
4,4'-DDD	1.6	4	12	32	80	160	32
4,4'-DDT	1.6	4	12	32	80	160	32
Mirex	1.6	4	12	32	80	160	32
Hexazinone	5	12.5	37.5	100	250	500	100
Methoxychlor	1.6	4	12	32	80	160	32
Endrin Ketone	1.6	4	12	32	80	160	32
Phosmet (Imidan)	10	25	75	200	500	1000	200
Azinphos-Methyl	5	12.5	37.5	100	250	500	100
Permethrins	2	5	15	40	100	200	40
Cypermethrins	10	25	75	200	500	1000	200
Surrogate Standards							Surrogate Standard Amount added to samples (ng)
¹³ C-HCB	86	86	86	86	86	86	32
D ₁₀ -Diazinon	77	77	77	77	77	77	32
¹³ C-Atrazine	77	77	77	77	77	77	32
¹³ C-gamma-HCH	130	130	130	130	130	130	52
¹³ C-Fonofos	77	77	77	77	77	77	32
¹³ C-Heptachlor	73	73	73	73	73	73	29
¹³ C-beta-HCH	77	77	77	77	77	77	32
¹³ C-delta-HCH	77	77	77	77	77	77	32
¹³ C-Aldrin	77	77	77	77	77	77	32
¹³ C-Oxychlordane	77	77	77	77	77	77	32
¹³ C-Heptachlor-Epoxide	79	79	79	79	79	79	32
¹³ C-t-Chlordane	77	77	77	77	77	77	32
¹³ C-t-Nonachlor	77	77	77	77	77	77	32
¹³ C ₉ -alpha-Endosulphan	77	77	77	77	77	77	32
¹³ C-Dieldrin	77	77	77	77	77	77	32
¹³ C-p,p-DDE	77	77	77	77	77	77	32
¹³ C ₁₂ -Endrin	77	77	77	77	77	77	32
¹³ C-c-Nonachlor	77	77	77	77	77	77	32
¹³ C ₉ -beta-Endosulphan	77	77	77	77	77	77	32
¹³ C-o,p-DDT	77	77	77	77	77	77	32
¹³ C-p,p-DDT	77	77	77	77	77	77	32
¹³ C-Mirex	84	84	84	84	84	84	32
¹³ C ₁₂ -Methoxychlor	77	77	77	77	77	77	32
D ₆ -Azinphos-Methyl	77	77	77	77	77	77	32
¹³ C-Permethrins	78	78	78	78	78	78	32
Recovery Standard							
¹³ C ₁₂ -PCB 52	80	80	80	80	80	80	80

¹ The level AA calibration standard solution is only used with "Clean Water" samples.

Concentration of Calibration Standard Solutions (ON Compounds)

	Concentration (ng/mL)					Authentic Standard Amount Added to sample (ng)
	A-Cal	B-Cal	C-Cal	D-Cal	E-Cal	
Native Compound						
Butylate	5	12	32	80	200	32
Ethalfuralin	55	132	352	880	2200	352
Trifluralin	5	12	32	80	200	32
Triallate	5	12	32	80	200	32
Dimethenamid	5	12	32	80	200	32
Alachlor	12	28.8	76.8	192	480	76.8
Methoprene	25	60	160	400	1000	160
Butralin	10	24	64	160	400	64
Flufenacet	8	19.2	51.2	128	320	51.2
Metolachlor	2.5	6	16	40	100	16
Linuron	20	48	128	320	800	128
Pendimethalin	40	96	256	640	1600	256
Flutriafol	50	120	320	800	2000	320
Tebuconazol	25	60	160	400	1000	160
Surrogate Standards						Surrogate Standard Amount added to samples (ng)
¹³ C-Alachlor	82	82	82	82	82	32
¹³ C-Metolachlor	80	80	80	80	80	32
D ₆ -Linuron	320	320	320	320	320	128
Recovery standard						
¹³ C ₁₂ PCB 52	80	80	80	80	80	80

ANALYTE IDENTIFICATION

A chromatographic peak is identified as a target compound if the following criteria are met for the quantification ion:

1. Peak responses must be at least three times the background noise level.
2. The relative retention time must be within the predicted window (refer to above tables "Analytes, Ions, and Quantification References").
3. Peak maxima for quantification and confirmation ions must coincide within two seconds.
4. The relative ion abundance ratios must be within the limits listed in the above tables "Analytes, Ions, and Quantification References". Some compounds' ion abundance ratios are determined theoretically based on naturally-occurring isotope abundances (ratios as listed), while some ratios are determined empirically based on the opening calibration verification standard (ratios are listed N/A), and some compounds are quantified using a single ion (ratio tolerances listed as N/A).

QUANTIFICATION

The response for any component is taken as the sum of the integrated peak areas for the two characteristic masses for that compound. Quantification is by the isotope dilution method. Target concentrations are determined with respect to either a labelled surrogate or the internal standard. Mean relative response factors (RRF), determined from either a multi-level initial calibration series or a mid-level calibration standard run at the beginning and end of the samples, are used to convert raw peak areas in sample chromatograms to final concentrations

$$\text{Concentration of Target} = \left(\frac{\text{area of Target}}{\text{area of Qt Std}} \right) \times \left(\frac{\text{weight of Qt Std (ng)}}{\text{RRF}} \right) \times \left(\frac{1}{\text{weight of sample (g or L)}} \right)$$

(ng/g or ng/L)

$$\text{where RRF} = \left(\frac{\text{area of Target}}{\text{area of Qt Std}} \right) \times \left(\frac{\text{concentration of Qt Std}}{\text{concentration of Target}} \right)$$

when no m1/m2 ratio exists:

area of Target = quantification ion peak area of the target

area of Qt Std = quantification ion peak area of the quantification standard

or when an m1/m2 ratio exists:

$$\text{area of Target} = \left(\frac{\text{Target quantification ion peak area}}{\text{m1/m2 ratio}} \right) + \text{Target quantification ion peak area}$$

$$\text{area of Qt Std} = \left(\frac{\text{Qt Std quantification ion peak area}}{\text{m1/m2 ratio}} \right) + \text{Qt Std quantification ion peak area}$$

and where the Qt Std is either the surrogate or the internal standard.

For target compounds quantified against the labelled standard added at the beginning of the analysis procedure, the results are recovery corrected by the method of quantification. Surrogate recoveries are determined similarly against the recovery (internal) standard and are used as general indicators of overall analytical quality. Analysis results for analytes that are quantified using the recovery standard are not recovery corrected.

REPORTING LIMITS

Concentrations and detection limits for the pesticides are reported. Typical reporting units for all data are ng/g, ng/L, or ng/sample. Concentrations for solids are reported on a dry weight basis. Concentrations in tissues are reported on a wet weight basis and/or on a lipid weight basis when requested. Concentrations in aqueous are reported on a volume basis. Concentrations in XAD-2 resin are reported on a per sample basis or a per volume basis.

The following are commonly requested reporting limits:

Sample Specific Detection Limit or Sample Detection Limit (SDL) – determined individually for every sample analysis run by converting the area equivalent of 3.0 times (2.5 times for EPA 1600 series methods) the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. The SDL accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up. Equivalent term: Estimated Detection Limit (EDL) from EPA method 8290.

Method Detection Limit (MDL) - determined as specified by EPA Fed. Reg. 40 CFR Part 136 Appendix B (no iteration option). The 99% confidence level MDL is determined based on analysis of a minimum of 7 replicate matrix spikes fortified at 1-10 times the estimated detection limit. MDL is determined as required based on accreditation, contract and workload requirements.

Lower Method Calibration Limit (LMCL) - determined by prorating the concentration of the lowest calibration limit for sample size and extract volume. The following equation is used. $((\text{lowest level cal conc.}) \times (\text{extract volume})) / \text{sample size}$. Typical extract volume for pesticides is 400 μL (500 μL for tissue extract).

For the analysis of pesticides AXYS standard is to report sample concentrations using the SDL as the reporting limit.

QUALITY ASSURANCE/QUALITY CONTROL

All samples are analyzed in batches with the following composition:

- Batch Size - Each batch consists of up to twenty test samples and additional QC samples.
- Blanks - One procedural blank is analyzed with each batch. The procedural blank is prepared by spiking an aliquot of the surrogate standard solution into a clean matrix and analyzed using the same procedures as the test samples in the analysis batch.
- On-going Precision and Recovery (OPR) Samples – On-going Precision and Recovery (OPR) is demonstrated by the analysis of a spiked reference matrix (SPM) analyzed with each batch. The reference sample to be analyzed is assigned to the analyst when the batch is assigned. The OPR sample is prepared by spiking an aliquot of the authentic spiking solution into an accurately weighed in-house reference matrix (known to contain low background levels of target analytes). The matrix is spiked with an aliquot of surrogate standard solution and, after an equilibration time of at least 30 minutes is extracted.
- Duplicates - Sample duplicates are analyzed (provided sufficient sample is available) for batches with 7-20 test samples, or when specified by the contract.
- Reference Samples – Certified reference materials are commercially available and are used to validate and periodically check methods. Additionally reference samples may be analyzed with a batch at the client's request.

The batch composition may vary according to batch or quality control requirements specified by a client. Each batch is carried through the complete analytical process as a unit. For sample data to be reportable the batch QC data must meet the acceptance criteria.

QC Specification Table: Authentic and Surrogate Standard Recoveries, OPR and Samples

Analyte	Blank Level	Laboratory Control Sample (OPR)		Surrogate
	(ng)	Recovery Range (%)		Recovery Range (%)
		Min.	Max.	
OCPs				
Aldrin	1	50	150	NA
Chlordane, alpha (cis)	1	50	150	NA
Nonachlor, cis-	1	50	150	NA
Heptachlor	1	50	150	NA
Oxychlordane	1	50	150	NA
Chlordane, gamma (trans)	1	50	150	NA
Nonachlor, trans-	1	50	150	NA
HCH, alpha	1	50	150	NA
HCH, beta	1	50	150	NA
HCH, gamma	1	50	150	NA
HCH, delta	1	50	150	NA
alpha-Endosulphan	1	50	150	NA
beta-Endosulphan	1	50	150	NA
Dieldrin	1	50	150	NA
Endosulphan-Sulphate	1	50	150	NA
Endrin	1	50	150	NA
Endrin-Ketone	1	20	150	NA
Heptachlor-Epoxyde	1	50	150	NA
Methoxychlor	1	50	150	NA
Captan	1	10	150	NA
Chlorothalonil	1	10	200	NA
Dacthal	1	40	150	NA
Hexachlorobenzene	1	50	150	NA
Mirex	1	50	150	NA
Octachlorostyrene	1	50	150	NA
Quintozerie	1	30	200	NA
Tecnazene	1	50	150	NA
o,p-DDE ²	1	50	150	NA
p,p-DDE ²	1	50	150	NA
o,p-DDD ²	1	50	150	NA
p,p-DDD, tissue matrix ²	1	20	150	NA
other matrices ²		50	150	NA
o,p-DDT	1	50	150	NA
p,p-DDT	1	50	150	NA
Perthane	1	50	150	NA
Triazines				
Ametryn, tissue matrix ¹	NA	NA	NA	NA
other matrices	1	20	200	NA
Atrazine	1	50	150	NA
Cyanazine	1	10	150	NA
Desethylatrazine	1	20	150	NA
Hexazinone	1	30	200	NA
Metribuzin	1	20	200	NA

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Simazine	1	50	150	NA
OPPs				
Azinphos-Methyl	1	50	150	NA
Chlorpyrifos	1	30	150	NA
Chlorpyrifos-Methyl	1	30	150	NA
Chlorpyrifos-Oxon	1	10	150	NA
Diazinon	1	50	150	NA
Diazinon-Oxon	1	10	300	NA
Dimethoate	1	50	250	NA
Disulfoton Sulfone ¹	NA	NA	NA	NA
Disulfoton ¹	NA	NA	NA	NA
Ethion	1	20	200	NA
Fenitrothion	1	30	150	NA
Fonofos	1	50	150	NA
Malathion, tissue matrix	1	20	150	NA
other matrices	1	50	150	NA
Methamidophos	1	20	150	NA
Parathion-Ethyl	1	50	150	NA
Parathion-Methyl	1	50	150	NA
Phorate ¹	1	5	150	NA
Phosmet	1	10	200	NA
Pirimiphos-Methyl	1	50	150	NA
Terbufos ¹	1	5	150	NA
ONs				
Alachlor	1	50	150	NA
Butralin	1	40	150	NA
Butylate	1	20	150	NA
Dimethenamid	1	40	150	NA
Ethalfuralin	1	30	150	NA
Flufenacet	1	30	150	NA
Flutriafol	1	20	150	NA
Linuron	1	50	150	NA
Methoprene, tissue matrix	1	20	150	NA
other matrices	1	50	150	NA
Metolachlor	1	50	150	NA
Pendimethalin	1	30	150	NA
Tebuconazol	1	20	200	NA
Triallate	1	20	150	NA
Trifluralin	1	40	150	NA
Pyrethroids				
Permethrin	1	50	150	NA
Cypermethrin	1	50	150	NA
Surrogates				
¹³ C-Aldrin	N/A	30	200	30-200
¹³ C-Nonachlor, cis-	N/A	30	200	30-200
¹³ C-Heptachlor	N/A	30	200	30-200
¹³ C-Oxychlorthane	N/A	30	200	30-200

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¹³ C-Chlordane, gamma (trans)	N/A	30	200	30-200
¹³ C-Nonachlor, trans-	N/A	30	200	30-200
¹³ C-HCH, beta	N/A	30	200	30-200
¹³ C-p,p-DDE	N/A	30	200	30-200
¹³ C-o,p-DDT	N/A	30	200	30-200
¹³ C-p,p-DDT	N/A	30	200	30-200
¹³ C-HCH, gamma	N/A	30	200	30-200
¹³ C-HCH, delta	N/A	30	200	30-200
¹³ C-alpha-Endosulphan	N/A	30	200	30-200
¹³ C-beta-Endosulphan	N/A	30	200	30-200
¹³ C-Dieldrin	N/A	30	200	30-200
¹³ C-Endrin	N/A	30	200	30-200
¹³ C-Heptachlor-Epoxyde	N/A	30	200	30-200
¹³ C-Methoxychlor	N/A	10	250	10-250
¹³ C-Hexachlorobenzene	N/A	20	200	20-200
¹³ C-Mirex	N/A	30	200	30-200
d ₆ -Azinphos-Methyl	N/A	50	300	30-300
d ₁₀ -Diazinon	N/A	30	200	30-200
¹³ C-Fonofos	N/A	30	200	30-200
¹³ C-Atrazine	N/A	30	200	30-200
¹³ C-trans-Permethrin	N/A	30	250	30-250
¹³ C-cis-Permethrin	N/A	30	250	30-250
¹³ C-Alachlor	N/A	30	200	30-200
d ₆ -Linuron	N/A	20	200	20-200
¹³ C-Metolachlor	N/A	30	200	30-200

¹ "Information value" only (estimated concentration; compound identity confirmed, but accuracy not established).

² o,p- and p,p-DDE and o,p- and p,p-DDD are reported as "Maximum values" due to potential formation from DDT degradation during analysis.

Failure of a analytical data to meet a cceptance criteria could lead to a repeat of the analysis or, where the data is judged fit for purpose, reporting with the appropriate qualification.

QC Specification Table: Other Parameters

QA Parameter	Specification
Duplicate	40% RPD for analytes above 10X detection limit
Bracketing Calibration	40% RSD for target analytes that are detected
Continuing Calibration (CAL/VER)	25% RSD for native analytes that have exact labelled standard and 35% for others
Linearity (ICAL)	25% RSD for native analytes that have exact labelled standard and 35% for others
Column resolution:	Gamma (trans)-chlordane and trans-nonachlor (or the labeled analogs) must be uniquely resolved to a valley height less than 10% of the shorter of the two peaks.
Retention Times	RRT windows are calculated from daily calibration verification run data using RRT references and fixed RT window brackets in seconds specified in the above tables "Analytes, Ions, and Quantification References".
Ion Ratios	Ion ratios must fall within the values specified in the above tables "Analytes, Ions, and Quantification References" for all targets and surrogates in the calibration standards (Levels A-E) and in the samples.
GC injector breakdown:	¹³ C ₁₂ -p,p-DDT breakdown must be ≤ 15%. ¹³ C ₁₂ -Endrin breakdown must be ≤ 20%.

Appendix N
Laboratory SOPs

AXYS SOP
MLA-010, Revision 10 Summary

Polychlorinated biphenyl (PCB) Congeners
By EPA 1668

Summary of AXYS Method MLA-010 Rev 10:

ANALYTICAL METHOD FOR THE DETERMINATION OF:

209 PCB CONGENERS BY EPA METHOD 1668A¹ OR EPA METHOD CBC01.2²

AXYS Method MLA-010 describes the analysis for the determination of the concentration of 209 PCB congeners in sediment, soil, sludge, tissue (including blood), aqueous samples, milk, solvent extracts, air samples and XAD columns.

Target Analytes

This analytical method determines the concentrations of all 209 PCB congeners by high resolution GC/MS (HRGC/HRMS). For EPA Method 1668A applications PCBs are reported using the congener numbering convention used in Method 1668A, for EPA Method CBC01.2 applications PCBs are reported using the congener numbering convention in EPA Method 1668B.

The concentrations of some PCB congeners are reported as the sum of two or more congeners due to coelution of the congeners. The coeluting congeners are listed below.

COELUTING PCB CONGENERS	
PCB 12, 13	PCB 93, 95, 98, 100, 102
PCB 30/18	PCB 107, 124
PCB 20, 28	PCB 110, 115
PCB 21, 33	PCB 128, 166
PCB 26, 29	PCB 129, 138, 160, 163
PCB 40, 41, 71	PCB 134, 143
PCB 44, 47, 65	PCB 135, 151, 154
PCB 45, 51	PCB 139, 140
PCB 49, 69	PCB 147, 149
PCB 50, 53	PCB 156, 157 ¹
PCB 59, 62, 75	PCB 153, 168
PCB 61, 70, 74, 76	PCB 171, 173
PCB 83, 99	PCB 183/185
PCB 85, 116, 117	PCB 180, 193
PCB 86, 87, 97 108, 119, 125	PCB 197/200
PCB 88, 91	PCB 198, 199
PCB 90, 101, 113	

¹ A second GC/MS analysis on a DB-1 column (30 m, 0.25 mm I.D., 0.25 µm film thickness) resolves the PCB 156/157 coeluting pair. This second analysis is performed upon request by the client.

The concentrations of all other PCB congeners are reported as the concentration of individual congeners.

A subset of congeners designated as “toxic” by the World Health Organization, can be reported with the associated toxic equivalents.

WHO TOXIC PCB CONGENERS	CONGENER NUMBER
3,4,4',5-Tetrachlorobiphenyl (TeCB)	81
3,3',4,4'-TCB	77
2,3,3',4,4'-Pentachlorobiphenyl (PeCB)	105
2,3,4,4',5-PeCB	114
2,3',4,4',5-PeCB	118
2',3,4,4',5-PeCB	123
3,3',4,4',5-PeCB	126
2,3,3',4,4',5-Hexachlorobiphenyl (HxCB)	156
2,3,3',4,4',5'-HxCB	157
2,3',4,4',5,5'-HxCB	167
3,3',4,4',5,5'-HxCB	169
2,3,3',4,4',5,5'-HpCB	189

Upon client request, any subset of the 209 PCB congeners may be reported.

EXTRACTION

All samples are spiked with ^{13}C -labelled surrogate standards prior to extraction and extracted as per the table below. Optional extraction procedures are shown within parentheses.

Sample Extraction

Matrix	Extraction
Aqueous	<p><1% solids Liquid-liquid extraction with dichloromethane.</p> <p>>1% solids sample is filtered prior to extraction and the particulate fraction separately extracted by Soxhlet extraction with dichloromethane. The filtrate is liquid-liquid extracted with dichloromethane. The two extracts are then combined.</p>
Solid (sediment, soil, sludge, particles on filter paper)	Soxhlet extraction with dichloromethane (optional: Dean-Stark Soxhlet extraction with toluene)
Tissue	Soxhlet extraction with dichloromethane (optional: Base digestion and liquid-liquid extraction with hexane)
Whole blood/serum	Liquid-liquid extraction with ethanol:hexane:saturated ammonium sulphate.
Milk	Liquid-liquid extraction with acetone and hexane.

XAD-2 column and filter	XAD-2 adsorbent is dried and extracted by Soxhlet with dichloromethane (optional Dean-Stark Soxhlet with toluene extraction). The filter is extracted by Dean-Stark Soxhlet extraction using toluene.
Ambient air (PUF and filter)	The PUF and filter(s) are Soxhlet extracted together using dichloromethane
Stationary Source Air Samples (Stack Gas sample trains)	The filter is sonicated with dilute hydrochloride acid and filtered. Equipment rinsates are collected, filtered, dried and/or extracted depending on sampling conditions.

COLUMN CHROMATOGRAPHY CLEANUP

Extracts are routinely cleaned up using the following chromatography columns:

- Multi-layered Acid/Base Silica
- Florisil
- Alumina

Extracts may be cleaned up using some or all of the following procedures as necessary:

- column chromatography on Biobeads
- column chromatography on 4.5% carbon/Celite

INSTRUMENTAL ANALYSIS

Instrumental analysis is performed on a SPB-Octyl column coupled to a high-resolution mass spectrometer (HRMS). The HRMS is operated at 8000 mass resolution throughout the mass range and 10000 for the center mass in each retention time window in the voltage selected ion-recording mode (V-SIR). Selected PFK ions are used as a reference for mass lock. Two masses from the molecular ion cluster are used to monitor each of the target analytes and ¹³C-labelled surrogate standards.

Upon client request resolution of the PCB 156/157 co-elution is achieved using a DB-1 chromatography column.

Analysis of the extract on either a DB-1 or DB-5 column is useful to resolve potential interferences with PCB 169 (from PCB 190).

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Table 6a. Nomenclature for EPA 1668A Applications

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
2 - MoCB	1	2051-60-7		11:34:00	1L	11:34:00	1.000	-1,3	0.999	1.004
3 - MoCB	2	2051-61-8		13:38:00	3L	13:48:00	0.988	6	0.984	0.992
4 - MoCB	3	2051-62-9		13:49:00	3L	13:48:00	1.001	-1,3	0.999	1.004
22' - DiCB	4	13029-08-8		14:04:00	4L	14:03:00	1.001	-1,3	0.999	1.004
26 - DiCB	10	33146-45-1		14:14:00	4L	14:03:00	1.013	6	1.009	1.017
25 - DiCB	9	34883-39-1		16:06:00	4L	14:03:00	1.146	6	1.142	1.149
24 - DiCB	7	33284-50-3		16:16:00	4L	14:03:00	1.158	6	1.154	1.161
23' - DiCB	6	25569-80-6		16:31:00	4L	14:03:00	1.176	6	1.172	1.179
23 - DiCB	5	16605-91-7		16:49:00	4L	14:03:00	1.197	6	1.193	1.200
24' - DiCB	8	34883-43-7		16:58:00	4L	14:03:00	1.208	6	1.204	1.211
35 - DiCB	14	34883-41-5		18:39:00	15L	20:08:00	0.926	6	0.924	0.929
33' - DiCB	11	2050-67-1		19:32:00	15L	20:08:00	0.970	6	0.968	0.973
34' - DiCB	13	2974-90-5	12 + 13							
34 - DiCB	12	2974-92-7	12 + 13	19:51:00	15L	20:08:00	0.986	6	0.983	0.988
44' - DiCB	15	2050-68-2		20:09:00	15L	20:08:00	1.001	-1,3	0.999	1.002
22'6 - TriCB	19	38444-73-4		17:15:00	19L	17:13:00	1.002	-1,3	0.999	1.003
246 - TriCB	30	35693-92-6	18 + 30							
22'5 - TriCB	18	37680-65-2	18 + 30	19:09:00	19L	17:13:00	1.112	6	1.109	1.115
22'4 - TriCB	17	37680-66-3		19:36:00	19L	17:13:00	1.138	6	1.136	1.141
23'6 - TriCB	27	38444-76-7		19:50:00	19L	17:13:00	1.152	6	1.149	1.155
236 - TriCB	24	55702-45-9		19:58:00	19L	17:13:00	1.160	6	1.157	1.163
22'3 - TriCB	16	38444-78-9		20:05:00	19L	17:13:00	1.167	6	1.164	1.169
24'6 - TriCB	32	38444-77-8		20:37:00	19L	17:13:00	1.197	6	1.195	1.200
2'35 - TriCB	34	37680-68-5		21:56:00	19L	17:13:00	1.274	6	1.271	1.277
235 - TriCB	23	55720-44-0		22:06:00	19L	17:13:00	1.284	6	1.281	1.287
245 - TriCB	29	15862-07-4	26 + 29							
23'5 - TriCB	26	38444-81-4	26 + 29	22:26:00	19L	17:13:00	1.303	10	1.298	1.308
23'4 - TriCB	25	55712-37-3		22:40:00	37L	27:27:00	0.826	6	0.824	0.828
24'5 - TriCB	31	16606-02-3		22:59:00	37L	27:27:00	0.837	6	0.835	0.839
244' - TriCB	28	7012-37-5	20 + 28							

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COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233' - TriCB	20	38444-84-7	20 + 28	23:18:00	37L	27:27:00	0.849	10	0.846	0.852
234 - TriCB	21	55702-46-0	21 + 33	23:30:00	37L	27:27:00	0.856	10	0.853	0.859
2'34 - TriCB	33	38444-86-9	21 + 33							
234' - TriCB	22	38444-85-8		23:57:00	37L	27:27:00	0.872	6	0.871	0.874
33'5 - TriCB	36	38444-87-0		25:35:00	37L	27:27:00	0.932	6	0.930	0.934
34'5 - TriCB	39	38444-88-1		25:58:00	37L	27:27:00	0.946	6	0.944	0.948
345 - TriCB	38	53555-66-1		26:33:00	37L	27:27:00	0.967	6	0.965	0.969
33'4 - TriCB	35	37680-69-6		27:03:00	37L	27:27:00	0.985	6	0.984	0.987
344' - TriCB	37	38444-90-5		27:28:00	37L	27:27:00	1.001	-1,3	0.999	1.002
22'66' - TeCB	54	15968-05-5		20:25:00	54L	20:25:00	1.000	-1,3	0.999	1.002
22'46 - TeCB	50	62796-65-0	50 + 53	22:41:00	54L	20:25:00	1.111	10	1.107	1.115
22'56' - TeCB	53	41464-41-9	50 + 53							
22'36 - TeCB	45	70362-45-7	45 + 51	23:24:00	54L	20:25:00	1.146	10	1.142	1.150
22'46' - TeCB	51	68194-04-7	45 + 51							
22'36' - TeCB	46	41464-47-5		23:41:00	54L	20:25:00	1.160	6	1.158	1.162
22'55' - TeCB	52	35693-99-3		25:11:00	54L	20:25:00	1.233	6	1.231	1.236
23'5'6 - TeCB	73	74338-23-1		25:20:00	54L	20:25:00	1.241	6	1.238	1.243
22'35 - TeCB	43	70362-46-8		25:26:00	54L	20:25:00	1.246	6	1.243	1.248
23'46 - TeCB	69	60233-24-1	49 + 69							
22'45' - TeCB	49	41464-40-8	49 + 69	25:40:00	54L	20:25:00	1.257	10	1.253	1.261
22'45 - TeCB	48	70362-47-9		25:59:00	54L	20:25:00	1.273	6	1.270	1.275
2356 - TeCB	65	33284-54-7	44 + 47 + 65							
22'44' - TeCB	47	2437-79-8	44 + 47 + 65							
22'35' - TeCB	44	41464-39-5	44 + 47 + 65	26:14:00	54L	20:25:00	1.285	10	1.281	1.289
2346 - TeCB	62	54230-22-7	59 + 62 + 75							
244'6 - TeCB	75	32598-12-2	59 + 62 + 75							
233'6 - TeCB	59	74472-33-6	59 + 62 + 75	26:34:00	54L	20:25:00	1.301	10	1.297	1.305
22'34' - TeCB	42	36559-22-5		26:45:00	54L	20:25:00	1.310	6	1.308	1.313
22'34 - TeCB	41	52663-59-9	40 + 41 + 71							
23'4'6 - TeCB	71	41464-46-4	40 + 41 + 71							
22'33' - TeCB	40	38444-93-8	40 + 41 + 71	27:14:00	54L	20:25:00	1.334	10	1.330	1.338
234'6 - TeCB	64	52663-58-8		27:31:00	54L	20:25:00	1.348	6	1.345	1.350
23'55' - TeCB	72	41464-42-0		28:24:00	81L	34:31:00	0.823	6	0.821	0.824

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COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
23'45' - TeCB	68	73575-52-7		28:42:00	81L	34:31:00	0.831	6	0.830	0.833
233'5' - TeCB	57	70424-67-8		29:09:00	81L	34:31:00	0.845	6	0.843	0.846
233'5' - TeCB	58	41464-49-7		29:23:00	81L	34:31:00	0.851	6	0.850	0.853
23'45' - TeCB	67	73575-53-8		29:34:00	81L	34:31:00	0.857	6	0.855	0.858
234'5' - TeCB	63	74472-34-7		29:50:00	81L	34:31:00	0.864	6	0.863	0.866
2345' - TeCB	61	33284-53-6	61 + 70 + 74 + 76	30:11:00	81L	34:31:00	0.874	12	0.872	0.877
23'4'5' - TeCB	70	32598-11-1	61 + 70 + 74 + 76							
2'345' - TeCB	76	70362-48-0	61 + 70 + 74 + 76							
244'5' - TeCB	74	32690-93-0	61 + 70 + 74 + 76							
23'44' - TeCB	66	32598-10-0		30:32:00	81L	34:31:00	0.885	6	0.883	0.886
233'4' - TeCB	55	74338-24-2		30:41:00	81L	34:31:00	0.889	6	0.887	0.890
233'4' - TeCB	56	41464-43-1		31:13:00	81L	34:31:00	0.904	6	0.903	0.906
2344' - TeCB	60	33025-41-1		31:27:00	81L	34:31:00	0.911	6	0.910	0.913
33'55' - TeCB	80	33284-52-5		31:54:00	81L	34:31:00	0.924	6	0.923	0.926
33'45' - TeCB	79	41464-48-6		33:29:00	81L	34:31:00	0.970	6	0.969	0.972
33'45' - TeCB	78	70362-49-1		34:05:00	81L	34:31:00	0.987	6	0.986	0.989
344'5' - TeCB	81	70362-50-4		34:32:00	81L	34:31:00	1.000	-1,3	1.000	1.001
33'44' - TeCB	77	32598-13-3		35:08:00	77L	35:07:00	1.000	-1,3	1.000	1.001
22'466' - PeCB	104	56558-16-8		26:10:00	104L	26:08:00	1.001	-1,3	0.999	1.002
22'366' - PeCB	96	73575-54-9		26:32:00	104L	26:08:00	1.015	10	1.012	1.018
22'45'6' - PeCB	103	60145-21-3		28:34:00	104L	26:08:00	1.093	6	1.091	1.095
22'356' - PeCB	94	73575-55-0		28:48:00	104L	26:08:00	1.102	6	1.100	1.104
22'35'6' - PeCB	95	38379-99-6	93 + 95 + 98 + 100 + 102							
22'44'6' - PeCB	100	39485-83-1	93 + 95 + 98 + 100 + 102							
22'356' - PeCB	93	73575-56-1	93 + 95 + 98 + 100 + 102	29:31:00	104L	26:08:00	1.129	20	1.123	1.136
22'456' - PeCB	102	68194-06-9	93 + 95 + 98 + 100 + 102							
22'3'46' - PeCB	98	60233-25-2	93 + 95 + 98 + 100 + 102							
22'346' - PeCB	88	55215-17-3	88 + 91	30:07:00	104L	26:08:00	1.152	12	1.149	1.156
22'34'6' - PeCB	91	68194-05-8	88 + 91							
22'33'6' - PeCB	84	52663-60-2		30:23:00	104L	26:08:00	1.163	6	1.161	1.165
22'346' - PeCB	89	73575-57-2		30:53:00	104L	26:08:00	1.182	6	1.180	1.184
23'45'6' - PeCB	121	56558-18-0		31:20:00	104L	26:08:00	1.199	6	1.197	1.201
22'355' - PeCB	92	52663-61-3		31:44:00	123L	37:12:00	0.853	6	0.852	0.854

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COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233'5'6 - PeCB	113	68194-10-5	90 + 101 + 113							
22'34'5 - PeCB	90	68194-07-0	90 + 101 + 113	32:19:00	123L	37:12:00	0.869	10	0.866	0.871
22'455' - PeCB	101	37680-73-2	90 + 101 + 113							
22'33'5 - PeCB	83	60145-20-2	83 + 99	32:53:00	123L	37:12:00	0.884	12	0.881	0.887
22'44'5 - PeCB	99	38380-01-7	83 + 99							
233'56 - PeCB	112	74472-36-9		33:04:00	123L	37:12:00	0.889	6	0.888	0.890
23'44'6 - PeCB	119	56558-17-9	86 + 87 + 97 + 108 + 119 + 125							
233'45' - PeCB	108	70362-41-3	86 + 87 + 97 + 108 + 119 + 125							
22'345 - PeCB	86	55312-69-1	86 + 87 + 97 + 108 + 119 + 125	33:29:00	123L	37:12:00	0.900	16	0.897	0.904
22'3'45 - PeCB	97	41464-51-1	86 + 87 + 97 + 108 + 119 + 125							
2'3456' - PeCB	125	74472-39-2	86 + 87 + 97 + 108 + 119 + 125							
22'345' - PeCB	87	38380-02-8	86 + 87 + 97 + 108 + 119 + 125							
234'56 - PeCB	117	68194-11-6	85 + 116 + 117							
23456 - PeCB	116	18259-05-7	85 + 116 + 117							
22'344' - PeCB	85	65510-45-4	85 + 116 + 117	34:12:00	123L	37:12:00	0.919	12	0.917	0.922
233'4'6 - PeCB	110	38380-03-9	110 + 115	34:27:00	123L	37:12:00	0.926	10	0.924	0.928
2344'6 - PeCB	115	74472-38-1	110 + 115							
22'33'4 - PeCB	82	52663-62-4		34:43:00	123L	37:12:00	0.933	6	0.932	0.935
233'55' - PeCB	111	39635-32-0		35:10:00	123L	37:12:00	0.945	6	0.944	0.947
23'455' - PeCB	120	68194-12-7		35:38:00	123L	37:12:00	0.958	6	0.957	0.959
233'4'5 - PeCB	107	70424-68-9	107 + 124	36:50:00	123L	37:12:00	0.990	10	0.988	0.992
2'3455' - PeCB	124	70424-70-3	107 + 124							
233'46 - PeCB	109	74472-35-8		37:05:00	123L	37:12:00	0.997	6	0.996	0.998
2'344'5 - PeCB	123	65510-44-3		37:13:00	123L	37:12:00	1.000	-1,3	1.000	1.001
233'45 - PeCB	106	70424-69-0		37:21:00	123L	37:12:00	1.004	6	1.003	1.005
23'44'5 - PeCB	118	31508-00-6		37:34:00	118L	37:32:00	1.001	-1,3	1.000	1.002
2'33'45 - PeCB	122	76842-07-4		37:55:00	118L	37:32:00	1.010	6	1.009	1.012
2344'5 - PeCB	114	74472-37-0		38:07:00	114L	38:06:00	1.000	-1,3	1.000	1.001
233'44' - PeCB	105	32598-14-4		38:48:00	105L	38:46:00	1.001	-1,3	0.999	1.001
33'455' - PeCB	127	39635-33-1		40:21:00	105L	38:46:00	1.041	6	1.040	1.042
33'44'5 - PeCB	126	57465-28-8		42:02:00	126L	42:01:00	1.000	-1,3	1.000	1.001
22'44'66' - HxCB	155	33979-03-2		32:06:00	155L	32:05:00	1.001	-1,3	0.999	1.002
22'3566' - HxCB	152	68194-09-2		32:17:00	155L	32:05:00	1.006	6	1.005	1.008

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COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
22'34'66' - HxCB	150	68194-08-1		32:28:00	155L	32:05:00	1.012	6	1.010	1.014
22'33'66' - HxCB	136	38411-22-2		32:51:00	155L	32:05:00	1.024	6	1.022	1.025
22'3466' - HxCB	145	74472-40-5		33:10:00	155L	32:05:00	1.034	6	1.032	1.035
22'34'56' - HxCB	148	74472-41-6		34:45:00	155L	32:05:00	1.083	6	1.082	1.085
22'355'6 - HxCB	151	52663-63-5	135 + 151 + 154							
22'33'56' - HxCB	135	52744-13-5	135 + 151 + 154	35:29:00	155L	32:05:00	1.106	10	1.103	1.109
22'44'5'6 - HxCB	154	60145-22-4	135 + 151 + 154							
22'345'6 - HxCB	144	68194-14-9		35:57:00	155L	32:05:00	1.121	6	1.119	1.122
22'34'56 - HxCB	147	68194-13-8	147 + 149	36:20:00	155L	32:05:00	1.132	10	1.130	1.135
22'34'5'6 - HxCB	149	38380-04-0	147 + 149							
22'33'56 - HxCB	134	52704-70-8	134 + 143	36:36:00	155L	32:05:00	1.141	10	1.138	1.143
22'3456' - HxCB	143	68194-15-0	134 + 143							
22'344'6 - HxCB	139	56030-56-9	139 + 140	36:58:00	155L	32:05:00	1.152	10	1.150	1.155
22'344'6' - HxCB	140	59291-64-4	139 + 140							
22'33'46 - HxCB	131	61798-70-7		37:11:00	155L	32:05:00	1.159	6	1.157	1.161
22'3456 - HxCB	142	41411-61-4		37:20:00	155L	32:05:00	1.164	6	1.162	1.165
22'33'46' - HxCB	132	38380-05-1		37:39:00	155L	32:05:00	1.174	10	1.171	1.176
22'33'55' - HxCB	133	35694-04-3		38:11:00	155L	32:05:00	1.190	6	1.189	1.192
233'55'6 - HxCB	165	74472-46-1		38:37:00	167L	43:57:00	0.879	6	0.878	0.880
22'34'55' - HxCB	146	51908-16-8		38:52:00	167L	43:57:00	0.884	6	0.883	0.885
233'45'6 - HxCB	161	74472-43-8		39:01:00	167L	43:57:00	0.888	6	0.887	0.889
22'44'55' - HxCB	153	35065-27-1	153 + 168	39:32:00	167L	43:57:00	0.900	10	0.898	0.901
23'44'5'6 - HxCB	168	59291-65-5	153 + 168							
22'3455' - HxCB	141	52712-04-6		39:43:00	167L	43:57:00	0.904	6	0.903	0.905
22'33'45' - HxCB	130	52663-66-8		40:08:00	167L	43:57:00	0.913	6	0.912	0.914
22'344'5 - HxCB	137	35694-06-5		40:22:00	167L	43:57:00	0.918	6	0.917	0.920
233'4'5'6 - HxCB	164	74472-45-0		40:29:00	167L	43:57:00	0.921	6	0.920	0.922
22'344'5' - HxCB	138	35065-28-2	129 + 138 + 160 + 163							
233'4'56 - HxCB	163	74472-44-9	129 + 138 + 160 + 163							
22'33'45 - HxCB	129	55215-18-4	129 + 138 + 160 + 163	40:53:00	167L	43:57:00	0.930	14	0.928	0.933
233'456 - HxCB	160	41411-62-5	129 + 138 + 160 + 163							

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COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233'44'6 - HxCB	158	74472-42-7		41:13:00	167L	43:57:00	0.938	6	0.937	0.939
2344'56 - HxCB	166	41411-63-6	128 + 166							
22'33'44' - HxCB	128	38380-07-3	128 + 166	42:08:00	167L	43:57:00	0.959	10	0.957	0.961
233'455' - HxCB	159	39635-35-3		43:10:00	167L	43:57:00	0.982	6	0.981	0.983
233'4'55' - HxCB	162	39635-34-2		43:28:00	167L	43:57:00	0.989	6	0.988	0.990
23'44'55' - HxCB	167	52663-72-6		43:59:00	167L	43:57:00	1.001	-1,3	1.000	1.001
233'44'5 - HxCB	156	38380-08-4		45:11:00	156L/157L	45:10:00	1.000	6	0.999	1.001
233'44'5' - HxCB	157	69782-90-7	156 + 157							
33'44'55' - HxCB	169	32774-16-6		48:36:00	169L	48:34:00	1.001	-1,3	1.000	1.001
22'34'566' - HpCB	188	74487-85-7		38:06:00	188L	38:04:00	1.001	-1,3	1.000	1.001
22'33'566' - HpCB	179	52663-64-6		38:26:00	188L	38:04:00	1.010	6	1.008	1.011
22'344'66' - HpCB	184	74472-48-3		39:00:00	188L	38:04:00	1.025	6	1.023	1.026
22'33'466' - HpCB	176	52663-65-7		39:22:00	188L	38:04:00	1.034	6	1.033	1.035
22'34566' - HpCB	186	74472-49-4		39:50:00	188L	38:04:00	1.046	6	1.045	1.048
22'33'55'6 - HpCB	178	52663-67-9		41:17:00	188L	38:04:00	1.085	6	1.083	1.086
22'33'45'6 - HpCB	175	40186-70-7		41:57:00	188L	38:04:00	1.102	6	1.101	1.103
22'34'55'6 - HpCB	187	52663-68-0		42:15:00	188L	38:04:00	1.110	6	1.109	1.111
22'344'56' - HpCB	182	60145-23-5		42:27:00	188L	38:04:00	1.115	6	1.114	1.116
22'344'5'6 - HpCB	183	52663-69-1	183 + 185	42:56:00	188L	38:04:00	1.128	6	1.127	1.129
22'3455'6 - HpCB	185	52712-05-7	183 + 185							
22'33'456' - HpCB	174	38411-25-5		43:07:00	188L	38:04:00	1.133	6	1.131	1.134
22'33'4'56 - HpCB	177	52663-70-4		43:35:00	188L	38:04:00	1.145	6	1.144	1.146
22'344'56 - HpCB	181	74472-47-2		44:00:00	188L	38:04:00	1.156	6	1.155	1.157
22'33'44'6 - HpCB	171	52663-71-5	171 + 173	44:13:00	188L	38:04:00	1.162	10	1.159	1.164
22'33'456 - HpCB	173	68194-16-1	171 + 173							
22'33'455' - HpCB	172	52663-74-8		45:57:00	189L	51:13:00	0.897	6	0.896	0.898
233'455'6 - HpCB	192	74472-51-8		46:15:00	189L	51:13:00	0.903	6	0.902	0.904
233'4'55'6 - HpCB	193	69782-91-8	180 + 193							
22'344'55' - HpCB	180	35065-29-3	180 + 193	46:36:00	180L	46:35:00	1.000	6	0.999	1.001
233'44'5'6 - HpCB	191	74472-50-7		47:00:00	189L	51:13:00	0.918	6	0.917	0.919
22'33'44'5 - HpCB	170	35065-30-6		47:57:00	170L	47:56:00	1.000	6	0.999	1.001

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COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233'44'56' - HpCB	190	41411-64-7		48:31:00	189L	51:13:00	0.947	6	0.946	0.948
233'44'55' - HpCB	189	39635-31-9		51:14:00	189L	51:13:00	1.000	-1,3	1.000	1.001
22'33'55'66' - OcCB	202	2136-99-4		43:43:00	202L	43:41:00	1.001	-1,3	1.000	1.001
22'33'45'66' - OcCB	201	40186-71-8		44:41:00	202L	43:41:00	1.023	10	1.021	1.025
22'344'566' - OcCB	204	74472-52-9		45:23:00	202L	43:41:00	1.039	6	1.038	1.040
22'33'44'66' - OcCB	197	33091-17-7	197 + 200	45:41:00	202L	43:41:00	1.046	6	1.045	1.047
22'33'4566' - OcCB	200	52663-73-7	197 + 200							
22'33'455'6 - OcCB	198	68194-17-2	198 + 199	48:40:00	202L	43:41:00	1.114	10	1.112	1.116
22'33'455'6' - OcCB	199	52663-75-9	198 + 199							
22'33'44'56' - OcCB	196	42740-50-1		49:23:00	205L	53:54:00	0.916	6	0.915	0.917
22'344'55'6 - OcCB	203	52663-76-0		49:35:00	205L	53:54:00	0.920	6	0.919	0.921
22'33'44'56 - OcCB	195	52663-78-2		50:59:00	205L	53:54:00	0.946	6	0.945	0.947
22'33'44'55' - OcCB	194	35694-08-7		53:26:00	205L	53:54:00	0.991	6	0.990	0.992
233'44'55'6 - OcCB	205	74472-53-0		53:56:00	205L	53:54:00	1.001	-1,3	1.000	1.001
22'33'455'66' - NoCB	208	52663-77-1		50:43:00	208L	50:42:00	1.000	-1,3	1.000	1.001
22'33'44'566' - NoCB	207	52663-79-3		51:42:00	208L	50:42:00	1.020	6	1.019	1.021
22'33'44'55'6 - NoCB	206	40186-72-9		55:45:00	206L	55:44:00	1.000	-1,3	1.000	1.001
22'33'44'55'66' - DeCB	209	2051-24-3		57:26:00	209L	57:25:00	1.000	-1,3	1.000	1.001
LABELLED COMPOUND										
13C12-2 - MoCB	1L			11:34:00	9L	16:05:00	0.719	30	0.704	0.735
13C12-4 - MoCB	3L			13:48:00	9L	16:05:00	0.858	30	0.842	0.874
13C12-22' - DiCB	4L			14:03:00	9L	16:05:00	0.874	30	0.858	0.889
13C12-44' - DiCB	15L			20:08:00	9L	16:05:00	1.252	30	1.236	1.267
13C12-22'6 - TriCB	19L			17:13:00	9L	16:05:00	1.070	30	1.055	1.086
13C12-344' - TriCB	37L			27:27:00	52L	25:09:00	1.091	30	1.082	1.101
13C12-22'66' - TeCB	54L			20:25:00	52L	25:09:00	0.812	20	0.805	0.818
13C12-33'44' - TeCB	77L			35:07:00	52L	25:09:00	1.396	20	1.390	1.403
13C12-344'5 - TeCB	81L			34:31:00	52L	25:09:00	1.372	20	1.366	1.379
13C12-22'466' - PeCB	104L			26:08:00	101L	32:19:00	0.809	20	0.804	0.814
13C12-233'44' - PeCB	105L			38:46:00	101L	32:19:00	1.200	20	1.194	1.205
13C12-2344'5 - PeCB	114L			38:06:00	101L	32:19:00	1.179	20	1.174	1.184
13C12-23'44'5 - PeCB	118L			37:32:00	101L	32:19:00	1.161	20	1.156	1.167
13C12-2'344'5 - PeCB	123L			37:12:00	101L	32:19:00	1.151	20	1.146	1.156

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COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
13C12-33'44'5' - PeCB	126L			42:01:00	101L	32:19:00	1.300	20	1.295	1.305
13C12-22'44'66' - HxCB	155L			32:05:00	138L	40:48:00	0.786	20	0.782	0.790
13C12-233'44'5' - HxCB and	156L			45:10:00	138L	40:48:00	1.107	20	1.103	1.111
13C12-233'44'5' - HxCB	157L									
13C12-23'44'55' - HxCB	167L			43:57:00	138L	40:48:00	1.077	20	1.073	1.081
13C12-33'44'55' - HxCB	169L			48:34:00	138L	40:48:00	1.190	20	1.186	1.194
13C12-22'34'566' - HpCB	188L			38:04:00	194L	53:25:00	0.713	20	0.710	0.716
13C12-233'44'55' - HpCB	189L			51:13:00	194L	53:25:00	0.959	20	0.956	0.962
13C12-22'33'55'66' - OcCB	202L			43:41:00	194L	53:25:00	0.818	20	0.815	0.821
13C12-233'44'55'6 - OcCB	205L			53:54:00	194L	53:25:00	1.009	30	1.004	1.014
13C12-22'33'44'55'6 - NoCB	206L			55:44:00	194L	53:25:00	1.043	30	1.039	1.048
13C12-22'33'455'66' - NoCB	208L			50:42:00	194L	53:25:00	0.949	20	0.946	0.952
13C12-22'344'55' - HpCB	180L			46:35:00	194L	53:25:00	0.872	20	0.869	0.875
13C12-22'33'44'5 - HpCB	170L			47:56:00	194L	53:25:00	0.897	20	0.894	0.900
13C12-22'33'44'55'66' - DeCB	209L			57:26:00	194L	53:25:00	1.075	30	1.071	1.080
LABELLED CLEAN-UP STANDARD										
13C12-244' - TriCB	28L			23:16:00	52L	25:09:00	0.925	20	0.918	0.932
13C12-233'55' - PeCB	111L			35:09:00	101L	32:19:00	1.088	20	1.083	1.093
13C12-22'33'55'6 - HpCB	178L			41:16:00	138L	40:48:00	1.011	20	1.007	1.016
LABELLED INJECTION INTERNAL STANDARD										
13C12-25 - DiCB	9L			16:05:00	138L	40:48:00	0.394	25	0.389	0.399
13C12-22'55' - TeCB	52L			25:09:00	138L	40:48:00	0.616	25	0.611	0.622
13C12-22'455' - PeCB	101L			32:19:00	138L	40:48:00	0.792	25	0.787	0.797
13C12-22'344'5' - HxCB	138L			40:48:00	138L	40:48:00	1.000	100	0.980	1.020
13C12-22'33'44'55' - OcCB	194L			53:25:00	138L	40:48:00	1.309	25	1.304	1.314
(1) Suffix "L" indicates labelled compound. (2) C = co-eluting congener										

Table 6b. Modifications to PCB Nomenclature for EPA CBC01.2 Applications **

COMPOUND	IUPAC NO.	CAS NO.	CO-ELUTIONS	COMPOUND RT	RT Reference	Labelled RT	RRT	RT Window (sec)	RRT Lower Limit	RRT Upper Limit
233'45' - PeCB	109	70362-41-3	86 + 87 + 97 + 109 + 119 + 125	33:29:00	123L	37:12:00	0.900	16	0.897	0.904
233'4'5 - PeCB	108	70424-68-9	108 + 124	36:50:00	123L	37:12:00	0.990	10	0.988	0.992
233'46 - PeCB	107	74472-35-8		37:05:00	123L	37:12:00	0.997	6	0.996	0.998

** Congeners named PCB 108, 107 and 109 in Method 1668A are named PCB 109, 108 and 107 respectively for EPA CBC01.2 applications

CALIBRATION

Initial calibration is performed using a five point calibration series of solutions that encompass the working concentration range. Initial calibration solutions contain the suite of labelled surrogate and recovery standards and natives listed in the table below. Calibration procedures use the mean RRFs determined from the initial calibration to calculate analyte concentrations. Calibration is verified at least once every 12 hours by analysis of a mid-level calibration solution. The mid level calibration solution contains 209 PCB congeners and is used to establish the relative response factors and retention times for those PCB congeners not present in the multi-level standards solutions.

Alternately clients may request initial calibration be performed using a six point calibration series of solutions if lower detection limits are required (CS 0.2).

Nominal Concentration of PCB Calibration Solutions

		Concentration (ng/mL)						
	Congener No. ¹	CS-0.2	CS-1	CS-2	CS-3	CS-4	CS-5	Native Standard Amount added to sample
Native Compounds								
2-MoCB	1	0.2	1.0	5.0	50	400	2000	1000 pg
4-MoCB	3	0.2	1.0	5.0	50	400	2000	1000 pg
2,2'-DiCB	4	0.2	1.0	5.0	50	400	2000	1000 pg
4,4'-DiCB	15	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',6-TriCB	19	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,5-TriCB	23	0.2	1.0	5.0	50	400	2000	1000 pg
2',3,5-TriCB	34	0.2	1.0	5.0	50	400	2000	1000 pg

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3,4,4'-TriCB	37	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',6,6'-TeCB	54	0.2	1.0	5.0	50	400	2000	1000 pg
3,3',4,4'-TeCB	77	0.2	1.0	5.0	50	400	2000	1000 pg
3,4,4',5'-TeCB	81	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',4,6,6'-PeCB	104	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,3',4,4'-PeCB	105	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,4,4',5'-PeCB	114	0.2	1.0	5.0	50	400	2000	1000 pg
2,3',4,4',5'-PeCB	118	0.2	1.0	5.0	50	400	2000	1000 pg
2',3,4,4',5'-PeCB	123	0.2	1.0	5.0	50	400	2000	1000 pg
3,3',4,4',5'-PeCB	126	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',4,4',6,6'-HxCB	155	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,3',4,4',5'-HxCB	156	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,3',4,4',5'-HxCB	157	0.2	1.0	5.0	50	400	2000	1000 pg
2,3',4,4',5,5'-HxCB	167	0.2	1.0	5.0	50	400	2000	1000 pg
3,3',4,4',5,5'-HxCB	169	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,3',4,4',5'-HpCB	170	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,4,4',5,5'-HpCB	180	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,4,4',5,6'-HpCB	182	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,4',5,5',6'-HpCB	187	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,4',5,6,6'-HpCB	188	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,3',4,4',5,5'-HpCB	189	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,3',5,5',6,6'-OxCB	202	0.2	1.0	5.0	50	400	2000	1000 pg
2,3,3',4,4',5,5',6'-OxCB	205	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,3',4,4',5,5',6'-NoCB	206	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,3',4,5,5',6,6'-NoCB	208	0.2	1.0	5.0	50	400	2000	1000 pg
2,2',3,3',4,4',5,5',6,6'-DeCB	209	0.2	1.0	5.0	50	400	2000	1000 pg
Surrogate Standards								Surrogate Standard Amount added to sample
¹³ C ₁₂ -2-MoCB	1L ²	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -4-MoCB	3L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2-DiCB	4L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -4,4'-DiCB	15L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -3,4,4'-TriCB	37L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',6,6'-TeCB	54L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -3,3',4,4'-TeCB	77L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -3,4,4',5'-TeCB	81L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',4,6,6'-PeCB	104L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,3,3',4,4'-PeCB	105L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,3,4,4',5'-PeCB	114L	100	100	100	100	100	100	2000 pg

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¹³ C ₁₂ -2,3',4,4',5-PeCB	118L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2',3,4,4',5-PeCB	123L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -3,3',4,4',5-PeCB	126L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',4,4',6,6'-HxCB	155L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,3,3',4,4',5-HxCB	156L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',3,3',4,4',5-HpCB	170L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',3,4',5,6,6'-HpCB	188L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',3,3',5,5',6,6'-OeCB	202L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,3,3',4,4',5,5',6-OeCB	205L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',3,3',4,5,5',6,6'-NoCB	208L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	100	100	100	100	100	2000 pg
Cleanup Standards								
¹³ C ₁₂ -2,4,4'-TriCB	28L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,3,3',5,5'-PeCB	111L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',3,3',5,5',6-HpCB	178L	100	100	100	100	100	100	2000 pg
Recovery Standards								
¹³ C ₁₂ -2,5-DiCB	9L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',5,5'-TeCB	52L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',4',5,5'-PeCB	101L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100	100	2000 pg
¹³ C ₁₂ -2,2',3,3',4,4',5,5'-OeCB	194L	100	100	100	100	100	100	2000 pg

1. Suffix "L" indicates labelled compound.

ANALYTE IDENTIFICATION

A chromatographic peak is identified as a target compound if the following criteria are met for the quantification and confirmation ions (where confirmation ions are available):

1. Peak responses must be at least 2.5 times the background noise level.
2. All peaks are acquired in the appropriate acquisition windows, when compared to the window standard.

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3. Peak centroids for the quantification and confirmation ions must coincide within two seconds.
4. The relative ion abundance ratios must be within 15% of the expected ratio.

Aroclor equivalent concentrations may be calculated by converting the summed concentrations of a suite of characteristic PCB congeners to concentrations using empirical factors determined from the analysis of Aroclor mixtures.

Aroclor 1016¹ = the sum of PCBs 8, 18/30, 31, 28/20 concentrations multiplied by 2.7;

Aroclor 1221 = the sum of PCBs 1, 3, 8 concentrations multiplied by 1.4;

Aroclor 1232 = the sum of PCBs 1, 3, 18/30 concentrations multiplied by 3.4;

Aroclor 1242¹ = the sum of PCBs 8, 18/30, 31, 28/20 concentrations multiplied by 3.0;

Aroclor 1248 = the sum of PCBs 44/47/65, 49/69, 66 concentrations multiplied by 6.1;

Aroclor 1254 = the sum of PCBs 86/87/97/108/119/125, 99 concentrations multiplied by 8.0;

Aroclor 1260 = the sum of PCBs 183/185, 180/193, 170 concentrations multiplied by 5.0;

Environmental samples with no clearly identified Aroclor signature are quantified as 1242/1254/1260 mixtures. Results may be reported as Aroclor 1248 instead of Aroclor 1242 and 1254 where the congener pattern clearly indicates this formulation. Other Aroclor formulations may be reported by calibration against the specific Aroclor solutions.

¹ Aroclors 1016 and 1242 may be reported as combined 1016/1242 using the 1242 factor

REPORTING LIMITS

Concentrations and detection limits for the 209 PCB congeners are reported. Typical reporting units for all data are pg/g, pg/L, or pg/sample. Concentrations for solids are reported on a dry weight basis. Concentrations in tissues (including blood and milk) are reported on a wet weight basis and/or on a lipid weight basis when requested. Concentrations in aqueous are reported on a volume basis. Concentrations in XAD-2 resin, filters and stack gas samples are reported on a per sample basis or a per volume basis. Concentrations in particulate filters are reported on a per sample basis.

The following are commonly requested reporting limits:

Sample Specific Detection Limit or Sample Detection Limit (SDL) – determined individually for every sample analysis run by converting the area equivalent of 2.5 times the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. The SDL accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up. Equivalent term(s): Estimated Detection Limit (EDL) from EPA method 8290.

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Method Detection Limit (MDL) - determined as specified by EPA Fed. Reg. 40 CFR Part 136 Appendix B (no iteration option). The 99% confidence level MDL is determined based on analysis of a minimum of 7 replicate matrix spikes fortified at 1-5 times the estimated detection limit. MDL is determined as required based on accreditation, contract and workload requirements.

Lower Method Calibration Limit (LMCL) - determined by prorating the concentration of the lowest calibration limit for sample size and extract volume. The following equation is used. $((\text{lowest level cal conc.}) \times (\text{extract volume})) / \text{sample size}$. Typical extract volume for PCBs is 20 μL .

For the analysis of PCBs AXYS standard is to report sample concentrations using the SDL with a minimum reporting limit of 0.5 pg absolute.

QUALITY ASSURANCE/QUALITY CONTROL

All samples are analyzed in batches with the following composition:

- Batch Size - Each batch consists of up to twenty test samples and additional QC samples.
- Blanks - One procedural blank is analyzed for each batch. The procedural blank is prepared by spiking an aliquot of the surrogate standard solution into a clean matrix.
- On-going Precision and Recovery (OPR) Samples – On-going Precision and Recovery (OPR) is demonstrated by the analysis of a spiked reference matrix (SPM) analyzed with each batch. The reference sample to be analyzed is assigned to the analyst when the batch is assigned. The OPR sample is prepared by spiking an aliquot of the authentic spiking solution into an accurately weighed in-house reference matrix (known to contain low background levels of target analytes). The matrix is spiked with an aliquot of surrogate standard solution and, after an equilibration time of at least 30 minutes is extracted.
- Duplicates - Sample duplicates are analyzed (provided sufficient sample is available) for batches with 7-20 test samples, or when specified by the contract. For some matrices (XAD columns, filters, air samples) only field duplicates (if available) can be analyzed.
- Reference Samples – Certified reference materials are commercially available and are used to validate and periodically check methods. Additionally reference samples may be analyzed with a batch at the client's request.

The batch composition may vary according to batch or quality control requirements specified by a client. Each batch is carried through the complete analytical process as a unit. For sample data to be reportable the batch QC data must meet the acceptance criteria.

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QC Specification Table: Native and Surrogate Standard Recoveries, CAL/VER, IPR, OPR, and Samples¹

Congener	Cong. No. ²	Test conc ng/mL	CAL/VER (%)		IPR (%)		OPR (%)		Labelled compound recovery in samples	
			Warning Limit	Acceptance Limit	RSD	X	Warning Limit	Acceptance Limit (%)	Warning Limit	Acceptance Limit
2-MoCB	1	50	75-125	70-130	40	60-140	70-130	50-150	-	-
4-MoCB	3	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2'-DiCB	4	50	75-125	70-130	40	60-140	70-130	50-150	-	-
4,4'-DiCB	15	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',6-TrCB	19	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,4,4'-TrCB	37	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',6,6'-TeCB	54	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4'-TeCB	77	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,4,4',5-TeCB	81	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',4,6,6'-PeCB	104	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4'-PeCB	105	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,4,4',5-PeCB	114	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3',4,4',5-PeCB	118	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2',3,4,4',5-PeCB	123	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4',5-PeCB	126	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',4,4',6,6'-HxCB	155	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5-HxCB ³	156	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5'-HxCB ³	157	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3',4,4',5,5'-HxCB	167	50	75-125	70-130	40	60-140	70-130	50-150	-	-
3,3',4,4',5,5'-HxCB	169	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,4',5,6,6'-HpCB	188	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5,5'-HpCB	189	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3',5,5',6,6'-OxCB	202	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,3,3',4,4',5,5',6-OxCB	205	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3',4,4',5,5',6-NoCB	206	50	75-125	70-130	40	60-140	70-130	50-150	-	-
2,2',3,3',4,5,5',6,6'-NoCB	208	50	75-125	70-130	40	60-140	70-130	50-150	-	-
DeCB	209	50	75-125	70-130	40	60-140	70-130	50-150	-	-
Labelled Compounds										
¹³ C ₁₂ -2-MoCB	1L	100	65-135	50-150	50	20-135	15-140	15-140	15-130	15-150
¹³ C ₁₂ -4-MoCB	3L	100	65-135	50-150	50	20-135	15-140	15-140	15-130	15-150
¹³ C ₁₂ -2,2'-DiCB	4L	100	65-135	50-150	50	35-135	30-140	30-140	25-130	25-150
¹³ C ₁₂ -4,4'-DiCB	15L	100	65-135	50-150	50	35-135	30-140	30-140	25-130	25-150
¹³ C ₁₂ -2,2',6-TrCB	19L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
¹³ C ₁₂ -3,4,4'-TrCB	37L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
¹³ C ₁₂ -2,2',6,6'-TeCB	54L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
¹³ C ₁₂ -3,3',4,4'-TCB	77L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
¹³ C ₁₂ -3,4,4',5-TeCB	81L	100	65-135	50-150	50	35-135	30-140	30-140	30-130	25-150
¹³ C ₁₂ -2,2',4,6,6'-PeCB	104L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,3,3',4,4'-PeCB	105L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,3,4,4',5-PeCB	114L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,3',4,4',5-PeCB	118L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150

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Congener	Cong. No. ²	Test conc ng/mL	CAL/VER (%)		IPR (%)		OPR (%)		Labelled compound recovery in samples	
¹³ C ₁₂ -2',3,4,4',5-PeCB	123L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -3,3',4,4',5-PeCB	126L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,2',4,4',6,6'-HxCB	155L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,3,3',4,4',5-HxCB ³	156L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,3,3',4,4',5'-HxCB ³	157L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,3',4,4',5,5'-HxCB	167L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -3,3',4,4',5,5'-HxCB	169L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
			Warning Limit	Acceptance Limit	RSD	X	Warning Limit	Acceptance Limit (%)	Warning Limit	Acceptance Limit
¹³ C ₁₂ -2,2',3,4',5,6,6'-HpCB	188L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2',3,3',4,4',5,5'-HpCB	189L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,2',3,3',5,5',6,6'-OcCB	202L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,3,3',4,4',5,5',6-OcCB	205L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,2',3,3',4,4',5,5',6-NoCB	206L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,2',3,3',4,5,5',6,6'-NoCB	208L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
¹³ C ₁₂ -2,2',3,3',4,4',5,5',6,6'-DeCB	209L	100	65-135	50-150	50	35-135	30-140	30-140	40-130	25-150
Cleanup Standard										
¹³ C ₁₂ -2,4,4'-TriCB	28L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135
¹³ C ₁₂ -2,3,3',5,5'-PeCB	111L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135
¹³ C ₁₂ -2,2',3,3',5,5',6-HpCB	178L	100	60-130	60-130	45	45-120	40-125	40-125	40-130	30-135

1. QC acceptance criteria for IPR, OPR, and samples based on a 20 µL extract final volume
2. Suffix "L" indicates labelled compound.
3. PCBs 156 and 157 are tested as the sum of two concentrations

QC Specification Table: QC Samples, Instrumental Analysis, and Analyte Quantification

QC Parameter	Specification
Analysis Duplicate Guideline	Agree to within $\pm 20\%$ of the mean (applicable to concentrations > 10 times the DL) ¹
Procedural Blank	Analyte concentrations in blank samples for PCB congeners 77, 81, 114, 123, 126 and 169 must be less than 2 pg/congener/sample, and concentrations of PCB congeners 156, 157, 167 and 189 must be less than 10 pg/congener/sample. Concentrations of all other individual PCB congeners or coelutions must be less than 50 pg/congener/sample in blank samples. The sum of all 209 congeners should be less than 300 pg/sample. Higher levels are acceptable where sample concentrations exceed 10 times the blank levels.
Sample Specific Detection Limit	Typical sample specific detection limits, determined from chromatographic noise, are in the range of 0.5 to 2.0 pg.
Initial Calibration	For 6-point calibration, a relative standard deviation of the RRF's $\leq 20\%$ for all compounds Ion ratios for all congeners must be within $\pm 15\%$ of theoretical for CS 0.2. Minimum S:N ratio 10:1 for all calibration standards. For CS0.2, S:N ratio may be as low as 3:1 for di-PCBs and nona-PCBs.
Continuing CAL VER	Refer to Table 4 above.
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Coders may use data from more than one chromatogram to get the responses in the calibrated range.
Ion Ratios	Ion ratios must fall within $\pm 15\%$ of the theoretical values for positive identification of all targets in the calibration standards and samples.
Sensitivity	Minimum S:N ratio 10:1 for all calibration standards. For CS0.2, S:N ratio may be as low as 3:1. for di-PCBs and nona-PCBs.

¹ Duplicate criterion is a guideline; final assessment depends upon sample characteristics, overall batch QC and on-going lab performance.

REFERENCES:

1. EPA Method 1668, Revision A - *Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, with changes and corrections through to August 20, 2003.*
2. EPA Method CBC01.2 *Statement of Work (SOW) for Analysis of Chlorinated Biphenyl Congeners (CBCS)*, December 2009.

APPENDIX A

SUMMARY OF MODIFICATIONS TO EPA METHOD 1668A

The following sections of EPA Method 1668A have been modified as described below.

Section 4.2.1, 4.2.2: The protocol for washing reusable glassware includes a detergent wash, water rinse and baking at a minimum of 300°C for 8 hours. Immediately prior to use, glassware is solvent rinsed with toluene and hexane.

Section 4.7: The first cleanup column for tissue extracts is a gravity gel permeation column (SX-3 Biobeads). An anthropogenic isolation column 7.5.3 is not used.

Section 6.5.1: Glass wool is cleaned by rinsing twice with toluene and twice with hexane.

Section 7.12, 7.13, 9.0, 11.0: The concentration of the labelled toxics/LOC and the cleanup standard spiking solutions is 100 ng/mL and the sample spiking volume is 20 µL. The resulting final concentrations in the extracts are as specified in the method.

Section 7.14: Concentration of the labelled injection internal standard spiking solution (recovery standard) is modified so that a volume of 5 µL is added. The resulting amount of standard added to the final extract is the same as specified in the method. The solution is spiked into a 15 µL extract volume for a final extract volume of 20 µL.

Section 7.2.1: Sodium sulphate is baked at a minimum of 300°C for 8 hrs rather than at 600°C for 24 hrs.

Section 7.5.1: Silica is activated by baking at 450°C in a muffle oven for at least 8 hrs.

Section 7.5.4.1.1: Florisil is baked at 450°C in a muffle oven for at least 8 hrs, then deactivated with water to 2.1% deactivation.

Section 10.3.3, 15.3.3: A S:N ratio of 3:1 for di-PCBs and nona-PCBs in CS0.2 calibration solution is acceptable.

Section 11.5.6: Unless requested by the client, the aqueous portion after filtration of aqueous samples with >1% solids is not discarded but is extracted.

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Section 11.5, 11.5.2, 11.5.5, 12.3 Solid samples are dried by mixing with anhydrous sodium sulphate. The dried solid is extracted using a soxhlet extraction apparatus. The surrogate spike is incorporated after the drying step. Equilibration time for the surrogate is 30 minutes. The extracting solvent for solids is dichloromethane.

Section 12.4, 11.8: The surrogate spike is incorporated into the sample after the drying step to eliminate the possibility of disproportional loss of volatile labelled and target compounds.

Section 12.4.2: The precleaning of the soxhlet apparatus is carried out using toluene instead of dichloromethane, for 2 hours.

Section 12.4.9: Lipid analysis is carried out by sub-sampling two 2 g portions of the extract from a total 30 g extract weight. The cleanup standard is spiked into the extract after soxhlet extraction and before any lipid analysis or rotary evaporation is done. The percent surrogate recoveries are corrected for the amount of extract used for lipid analysis.

Section 12.6.1.1: Rotary evaporation is done at 30°C. Daily cleaning of the rotary evaporators include dismantling and rinsing/soaking with solvent. Mimic proofs are run periodically but are not archived daily.

Section 12.7.4: Before Florisil or alumina cleanup procedures, a solvent exchange is done by reducing under nitrogen to 300 uL and bulking up to 1mL in hexane. If toluene is present the extract is reduced to 50 uL under nitrogen and bulked up to 1mL.

Section 12.7.7: Toluene (1 mL) is added to the eluate from the final column prior to rotary evaporation and nitrogen blow down concentration steps.

Section 13.1.1: GPC chromatography, by a gravity column, is routinely used only for tissue extracts. The GPC cleanup is optional for all other matrices.

Section 13.3.1: Routine layered silica column is as follows: 0.5 g neutral silica, 2 g 28% basic silica, 0.5 g neutral silica, 4 g 44% acidic silica, 4 g 22% acidic silica, 1 g neutral silica.

Section 13.3.4: The sample is loaded onto the column followed by 2-3 rinses of a least 1 mL, and eluted with 100mL of hexane.

Section 14.2: The volume of labelled injection internal standard (recovery standard) added to the extract is 5 µL, for a final extract volume of 20 µL. Hexane rather than nonane is used as the solvent to bring extract back to volume for re-analysis or to dilute extracts.

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Section 15.3: The calibration solution containing all 209 PCB congeners is used as the CAL/VER solution.

Section 17.5: Extracts are diluted with hexane. The concentration of the labelled injection internal (recovery) standard is not re-adjusted to 100 pg/uL when dilutions are performed.

Section 17.0

Conc_i - the concentrations of target analytes, and the labelled compound concentrations and recoveries, are calculated using the equations below. These procedures are equivalent to those described in the method but are more direct.

$$Conc_i = \frac{A_i}{A_{si}} \times \frac{M_{si}}{RRF_{i,si}} \times \frac{1}{M_x}$$

- where A_i = summed areas of the primary and secondary m/z's for the analyte peak of interest (compound *i*)
 A_{si} = summed areas of the primary and secondary m/z's for the labelled surrogate peak used to quantify *i*)
 M_x = mass of sample taken for analysis
 M_{si} = mass of labelled surrogate (compound *si*) added to sample as calculated by the concentration of standard spiked (pg/mL) multiplied by the volume spiked (mL)
 $RRF_{i,si}$ = mean relative response factor of *i* to *si* from the five-point calibration range and defined individually as:

$$\frac{A_i}{A_{si}} \times \frac{M_{si}}{M_i}$$

Calculation of Surrogate Standard Concentrations and Percent Recoveries:

Concentrations of surrogate standards are calculated using the following equation:

$$Conc_{si} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}}$$

and, the percent recoveries of the surrogate standards are calculated using the following equation:

$$\%Recovery = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}} \times \frac{1}{M_{si}} \times 100$$

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where A_{rs} and A_{si} are the summed peak areas (from the primary and secondary m/z channels) of recovery standard and labelled surrogate added to the sample;

M_{rs} and M_{si} are the masses of recovery standard and labelled surrogate added to the sample, and;

$RRF_{si,rs}$ is the mean relative response factor of the labelled surrogate to the recovery standard as determined by the five-point calibration range and defined individually as:

$$\frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{M_{si}}$$

Appendix N
Laboratory SOPs

AXYS SOP
MLA-017, Revision 20 Summary

Dioxin and Furans (PCDD/PCDF)
By EPA 1613B

Summary of AXYS Method MLA-017 Rev 20:

ANALYTICAL METHOD FOR THE DETERMINATION OF

POLYCHLORINATED DIBENZODIOXINS AND

DIBENZOFURANS

BY

EPA METHOD 1613B¹, EPA METHOD 8290²/8290A³,

ENV. CANADA EPS 1/RM/19⁴ OR EPA METHOD DLM02.2⁵

AXYS Method MLA-017 describes the analysis of polychlorinated (tetra-octa) dibenzodioxins and dibenzofurans in solids (sediment, soil, pulp, sludge), tissues (including milk and blood), aqueous samples, XAD-2 columns, air samples, particulate filters and solvent extracts.

Target Analytes

Dioxins (PCDD)	Furans (PCDF)
2,3,7,8 Tetrachlorodibenzodioxin (TCDD)	2,3,7,8 Tetrachlorodibenzofuran (TCDF)
Total TCDD	Total TCDF
1,2,3,7,8 Pentachlorodibenzodioxin (PeCDD)	1,2,3,7,8 Pentachlorodibenzofuran (PeCDF)
Total PeCDD	2,3,4,7,8 PeCDF
	Total PeCDF
1,2,3,4,7,8 Hexachlorodibenzodioxin (HxCDD)	1,2,3,4,7,8 Hexachlorodibenzofuran (HxCDF)
1,2,3,6,7,8 HxCDD	1,2,3,6,7,8 HxCDF
1,2,3,7,8,9 HxCDD	1,2,3,7,8,9 HxCDF
Total HxCDD	2,3,4,6,7,8 HxCDF
	Total HxCDF
1,2,3,4,6,7,8 Heptachlorodibenzodioxin (HpCDD)	1,2,3,4,6,7,8 Heptachlorodibenzofuran (HpCDF)
Total HpCDD	1,2,3,4,7,8,9 HpCDF
	Total HpCDF
Octachlorodibenzodioxin (OCDD)	Octachlorodibenzofuran (OCDF)

EXTRACTION

All samples are spiked with ^{13}C -labelled surrogate standards prior to extraction and extracted as per the table below. Optional extraction procedures are shown within parentheses.

Sample Extraction

Matrix	Extraction
Aqueous	Liquid-liquid extraction with dichloromethane. (If visible particulates are present the sample is filtered prior to extraction and the particulate fraction separately extracted by Soxhlet extraction or Dean-Stark Soxhlet extraction. The two extracts are then combined.)
Solid (sediment, soil, sludge, particles on filter paper)	Soxhlet extraction with toluene:acetone 80:20. (optional: Dean-Stark Soxhlet extraction with toluene)
Solid (pulp, black liquor)	Soxhlet extraction with toluene:acetone 80:20.
Solid (ash, slag)	Sonication with hydrochloric acid and filtering. Liquid-liquid extraction of filtrate using dichloromethane, Soxhlet extraction of particulate using toluene:acetone 80:20. The two extracts are combined.
Tissue	Soxhlet extraction with dichloromethane:hexane 1:1 (optional: Base digestion and liquid-liquid extraction with hexane)
Whole blood/serum	Liquid-liquid extraction with ethanol:hexane:saturated ammonium sulphate.
Milk	Liquid-liquid extraction with acetone and hexane.
XAD-2 column and filter	XAD-2 adsorbent is dried and extracted by Soxhlet (with toluene:acetone 80:20) or Dean-Stark Soxhlet (with toluene) extraction. The filter is extracted by Dean-Stark Soxhlet extraction using toluene.
Ambient air (PUF and filter)	The PUF and filter(s) are Soxhlet extracted together using toluene:acetone 80:20.
Stationary Source Air Samples (Stack Gas sample trains)	The filter is sonicated with dilute hydrochloride acid and filtered. Equipment rinsates are collected, filtered, dried and/or extracted depending on sampling conditions.

COLUMN CHROMATOGRAPHY CLEANUP

Extracts are routinely cleaned up manually, by an automated fluid management (FMS) system, or by using a combined ("hybrid") manual and FMS cleanup procedure according to the following table:

Water Soil Sediment XAD-2 adsorbent Air samples	<p>1) <u>Hybrid</u>: (M B/A wash →) M Extra-Large Layered Silver Nitrate/Acid/Base Silica Column → F Alumina → F Carbon/Celite</p> <p>2) <u>Full FMS</u>: (M B/A wash →) F Jumbo Layered Silica Columns → F Small Layered Silica Columns → F Alumina → F Carbon/Celite</p> <p>3) <u>Manual</u>: M Small Layered Silver Nitrate/Acid/Base Silica → M Alumina → M Copper → M Carbon/Celite (→ M Florisil)</p>
Sludge High organic soil	<p>1) <u>Hybrid</u>: (M B/A wash →) M Extra-Large Layered Silver Nitrate/Acid/Base Silica Column → F Alumina → F Carbon/Celite</p> <p>2) <u>Full FMS</u>: (M B/A wash →) F Jumbo Layered Silica Columns → F Small Layered Silica Columns → F Alumina → F Carbon/Celite</p> <p>3) <u>Manual</u>: (M Biobead →) M Large Layered Silver Nitrate/Acid/Base Silica → M Alumina → M Copper → M Carbon/Celite (→ M Florisil)</p>
Tissue Blood Milk	<p>1) <u>Full FMS</u>: (M Biobead →) F Jumbo Acid Silica Column → F Small Layered Silica Columns → F Alumina → F Carbon/Celite</p> <p>2) <u>Manual</u>: M Biobead → M Small Layered Acid/Base Silica → M Alumina → (M Copper →) M Carbon/Celite (→ M Florisil)</p>

Notes:

Options listed as 1) in the table above are the current default options. Items in brackets are optional procedures that may be used if needed or if required by Project Managers.

M = Manual column or cleanup step

F = FMS column

An optional Biobead clean-up may be carried out for biosolid sample extracts.

INSTRUMENTAL ANALYSIS

Instrumental analysis is performed on a DB-5 capillary chromatography column coupled to a high-resolution mass spectrometer (HRMS). The HRMS is operated at a static (10000) mass resolution in the voltage selected ion-recording mode (V-SIR) using selected PFK ions as a reference for mass lock. Two masses from the molecular ion cluster are used to monitor each of the target analytes and ¹³C-labelled surrogate standards. A second column DB-225 is used for confirmation of 2,3,7,8-TCDF identification. Five additional ions are monitored to check for interference from chlorinated diphenylethers.

Upon client request, the concentrations of PCDD/F may be determined using bracketing calibration procedures and a smaller suite of surrogate standards.

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Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans

Analytes	Quantification Ion (m/z)	Confirmation Ion (m/z)	Surrogate	RRF Determined From
2,3,7,8-TCDD	320	322	¹³ C ₁₂ -2,3,7,8-TCDD	2,3,7,8-TCDD
1,3,6,8-TCDD *	320	322	¹³ C ₁₂ -2,3,7,8-TCDD	2,3,7,8-TCDD
1,3,7,9-TCDD *	320	322	¹³ C ₁₂ -2,3,7,8-TCDD	2,3,7,8-TCDD
1,2,3,7,8-PeCDD	354	356	¹³ C ₁₂ -1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	390	392	¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD	390	392	¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	390	392	Mean of ¹³ C ₁₂ -1,2,3,6,7,8/1,2,3,4,7,8-HxCDD	1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD	424	426	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD
OCDD	458	460	¹³ C ₁₂ -OCDD	OCDD
2,3,7,8-TCDF	304	306	¹³ C ₁₂ -2,3,7,8 -TCDF	2,3,7,8-TCDF
1,2,7,8-TCDF *	304	306	¹³ C ₁₂ -2,3,7,8 -TCDF	2,3,7,8-TCDF
1,2,3,7,8-PeCDF	340	342	¹³ C ₁₂ -1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	340	342	¹³ C ₁₂ -2,3,4,7,8-PeCDF	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF	374	376	¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF	374	376	¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	374	376	¹³ C ₁₂ -2,3,4,6,7,8-HxCDF	2,3,4,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	374	376	¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDF	408	410	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	408	410	¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	1,2,3,4,7,8,9-HpCDF
OCDF	442	444	¹³ C ₁₂ -OCDD	OCDF
Cleanup Standard				
³⁷ Cl ₄ -2,3,7,8-TCDD	328	-	¹³ C ₁₂ -1,2,3,4-TCDD	
Labelled Surrogates	Quantification Ion (m/z)	Confirmation Ion (m/z)	Recovery Calculated Using	
¹³ C ₁₂ -2,3,7,8-TCDD	332	334	¹³ C ₁₂ -1,2,3,4-TCDD	
¹³ C ₁₂ -1,2,3,7,8-PeCDD	366	368	¹³ C ₁₂ -1,2,3,4-TCDD	
¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	402	404	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	402	404	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	436	438	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -OCDD	470	472	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -2,3,7,8 -TCDF	316	318	¹³ C ₁₂ -1,2,3,4-TCDD	
¹³ C ₁₂ -1,2,3,7,8-PeCDF	352	354	¹³ C ₁₂ -1,2,3,4-TCDD	
¹³ C ₁₂ -2,3,4,7,8-PeCDF	352	354	¹³ C ₁₂ -1,2,3,4-TCDD	
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	384	386	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	384	386	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	384	386	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -2,3,4,6,7,8-HpCDF	384	386	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	418	420	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	418	420	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
Recovery Stds				
¹³ C ₁₂ -1,2,3,4-TCDD	332	334	*Optional isomers which may be reported upon client request.	
¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	402	404		

CALIBRATION

Initial calibration is performed using a five point calibration series of solutions that encompass the working concentration range. Initial calibration solutions contain the suite of labelled surrogate and recovery standards and authentic target PCDDs/PCDFs. Calibration is verified at least once every 12 hours by an analysis of a mid-level calibration solution. Calibration procedures use the mean RRFs determined from the initial calibration to calculate analyte concentrations.

Alternately clients may request initial calibration be performed using a six point calibration series of solutions if lower detection limits are required.

Concentration of PCDD/PCDF Calibration Solutions

	Concentration (ng/mL)						Authentic Standard Amount added to sample (pg)
	CS0.2	CS1	CS2	CS3	CS4	CS5	
Native Compound							
2,3,7,8-TCDD	0.1	0.5	2	10	40	200	200
2,3,7,8-TCDF	0.1	0.5	2	10	40	200	200
1,2,3,7,8-PeCDD	0.5	2.5	10	50	200	1000	1000
1,2,3,7,8-PeCDF	0.5	2.5	10	50	200	1000	1000
2,3,4,7,8-PeCDF	0.5	2.5	10	50	200	1000	1000
1,2,3,4,7,8-HxCDD	0.5	2.5	10	50	200	1000	1000
1,2,3,6,7,8-HxCDD	0.5	2.5	10	50	200	1000	1000
1,2,3,7,8,9-HxCDD	0.5	2.5	10	50	200	1000	1000
1,2,3,4,7,8-HxCDF	0.5	2.5	10	50	200	1000	1000
1,2,3,6,7,8-HxCDF	0.5	2.5	10	50	200	1000	1000
1,2,3,7,8,9-HxCDF	0.5	2.5	10	50	200	1000	1000
2,3,4,6,7,8-HxCDF	0.5	2.5	10	50	200	1000	1000
1,2,3,4,6,7,8-HpCDD	0.5	2.5	10	50	200	1000	1000
1,2,3,4,6,7,8-HpCDF	0.5	2.5	10	50	200	1000	1000
1,2,3,4,7,8,9-HpCDF	0.5	2.5	10	50	200	1000	1000
OCDD	1.0	5.0	20	100	400	2000	2000
OCDF	1.0	5.0	20	100	400	2000	2000
Surrogate Standards							Surrogate Standard Amount added to sample (pg)
¹³ C ₁₂ -2,3,7,8-TCDD	100	100	100	100	100	100	2000
¹³ C ₁₂ -2,3,7,8-TCDF	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,7,8-PeCDD	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,7,8-PeCDF	100	100	100	100	100	100	2000
¹³ C ₁₂ -2,3,4,7,8-PeCDF	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	100	100	100	100	100	100	2000

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¹³ C ₁₂ -2,3,4,6,7,8-HxCDF	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	100	2000
¹³ C ₁₂ -OCDD	200	200	200	200	200	200	4000
Cleanup Standard							
³⁷ Cl ₄ -2,3,7,8-TCDD	0.1	0.5	2	10	40	200	200
Recovery Standard							
¹³ C ₁₂ -1,2,3,4-TCDD	100	100	100	100	100	100	2000
¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	100	100	100	100	100	100	2000

ANALYTE IDENTIFICATION

A chromatographic peak is identified as a target compound if the following criteria are met for the quantification and confirmation ions (where confirmation ions are available):

1. Peak responses must be at least 2.5 times the background noise level.
2. All peaks are acquired in the appropriate acquisition windows, when compared to the window standard.
3. Peak centroids for the quantification and confirmation ions must coincide within two seconds.
4. The relative ion abundance ratios must be within 15% of the expected ratio.

QUANTIFICATION

The response for any component is taken as the sum of the integrated peak areas for the two characteristic masses for that compound. Quantification is by the isotope dilution method. Target concentrations are determined with respect to labelled surrogate standards. Mean relative response factors (RRF), determined from the multi-level initial calibration series are used to convert raw peak areas in sample chromatograms to final concentrations as follows:

$$\text{Concentration of Target} = \left(\frac{\text{area of Target}}{\text{area of Qt Std}} \right) \times \left(\frac{\text{weight of Qt Std}}{\text{RRF}} \right) \times \left(\frac{1}{\text{weight of sample}} \right)$$

$$\text{where RRF} = \left(\frac{\text{area of Target}}{\text{area of Qt Std}} \right) \times \left(\frac{\text{weight of Qt Std}}{\text{weight of Target}} \right)$$

and the Qt Std is either the surrogate or the internal standard

Those compounds quantified against a labelled standard added at the beginning of the analysis procedure are recovery corrected by the method of quantification. Surrogate recoveries are determined similarly against the recovery (internal) standard and are used as general indicators of overall analytical quality.

REPORTING LIMITS

Concentrations and detection limits for the 2,3,7,8-polychlorinated dioxins and furans (tetra-octa) are reported. Typical reporting units for all data are pg/g, pg/L or pg/sample. Concentrations for solids are reported on a dry weight basis. Concentrations in tissues (including blood and milk) are reported on a wet weight basis and/or on a lipid weight basis when requested. Concentrations in aqueous samples are reported on a volume basis. Concentrations in XAD-2 resin, filters and stack gas samples are reported on a per sample basis or a per volume basis. Concentrations in particulate filters are reported on a per sample basis.

The following are commonly requested reporting limits:

Sample Specific Detection Limit or Sample Detection Limit (SDL) – determined individually for every sample analysis run by converting the area equivalent of 3.0 times (2.5 times for EPA 1600 series methods) the estimated chromatographic noise height to a concentration in the same manner that target peak responses are converted to final concentrations. The SDL accounts for any effect of matrix on the detection system and for recovery achieved through the analytical work-up. Equivalent term(s): Estimated Detection Limit (EDL) from EPA method 8290.

Method Detection Limit (MDL) - determined as specified by EPA Fed. Reg. 40 CFR Part 136 Appendix B (no iteration option). The 99% confidence level MDL is determined based on analysis of a minimum of 7 replicate matrix spikes fortified at 1-10 times the estimated detection limit. MDL is determined as required based on accreditation, contract and workload requirements.

Lower Method Calibration Limit (LMCL) - determined by prorating the concentration of the lowest calibration limit for sample size and extract volume. The following equation is used. $((\text{lowest level cal conc.}) \times (\text{extract volume})) / \text{sample size}$. Typical extract volume for PCDDs/PCDFs is 20 µL.

For the analysis of PCDDs/PCDFs AXYS standard is to report sample concentrations using the SDL with a minimum reporting limit of 0.5 pg absolute.

QUALITY ASSURANCE/QUALITY CONTROL

All samples are analyzed in batches with the following composition:

- Batch Size - Each batch consists of up to twenty test samples and additional QC samples.
- Blanks - One procedural blank is analyzed for each batch. The procedural blank is prepared by spiking an aliquot of the surrogate standard solution into a clean matrix.
- On-going Precision and Recovery (OPR) Samples – On-going Precision and Recovery (OPR) is demonstrated by the analysis of a spiked reference matrix (SPM) analyzed with each batch. The reference sample to be analyzed is assigned to the analyst when the batch is assigned. The OPR sample is prepared by spiking an aliquot of the authentic spiking solution into an accurately weighed in-house reference matrix (known to contain low background levels of target analytes). The matrix is spiked with an aliquot of surrogate standard solution and, after an equilibration time of at least 30 minutes is extracted.

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- Duplicates - Sample duplicates are analyzed (provided sufficient sample is available) for batches with 7-20 test samples, or when specified by the contract. For some matrices (XAD columns, filters, air samples) only field duplicates (if available) can be analyzed.
- Reference Samples – Certified reference materials are commercially available and are used to validate and periodically check methods. Additionally reference samples may be analyzed with a batch at the client's request.

The batch composition may vary according to batch or quality control requirements specified by a client. Each batch is carried through the complete analytical process as a unit. For sample data to be reportable the batch QC data must meet the acceptance criteria.

QC Specification Table: Authentic and Surrogate Standard Recoveries, CAL/VER, IPR, OPR and Samples

	Test Conc. (ng/mL)	IPR		OPR (%)	I-CAL (%)	CAL/VER (%)	Labelled Compound % Rec. in Sample		
		SD (%) *	\bar{X} (%)				Warning Limits	Control Limits	EPS 1/RM/19 Limits
Native Compound									
2,3,7,8-TCDD	10	28	83-129	70-130	20	78-125	-	-	-
2,3,7,8-TCDF	10	20	87-137	75-130	20	84-120	-	-	-
1,2,3,7,8-PeCDD	50	15	76-132	70-130	20	78-125	-	-	-
1,2,3,7,8-PeCDF	50	15	86-124	80-130	20	82-120	-	-	-
2,3,4,7,8-PeCDF	50	17.2	72-150	70-130	20	82-122	-	-	-
1,2,3,4,7,8-HxCDD	50	18.8	78-152	70-130	20	78-125	-	-	-
1,2,3,6,7,8-HxCDD	50	15.4	84-124	76-130	20	78-125	-	-	-
1,2,3,7,8,9-HxCDD	50	22.2	74-142	70-130	35	82-122	-	-	-
1,2,3,4,7,8-HxCDF	50	17.4	82-118	72-130	20	90-112	-	-	-
1,2,3,6,7,8-HxCDF	50	13.4	92-120	84-130	20	88-114	-	-	-
1,2,3,7,8,9-HxCDF	50	12.8	84-122	78-130	20	90-112	-	-	-
2,3,4,6,7,8-HxCDF	50	14.8	74-148	70-130	20	88-114	-	-	-
1,2,3,4,6,7,8-HpCDD	50	15.4	76-130	70-130	20	86-116	-	-	-
1,2,3,4,6,7,8-HpCDF	50	12.6	90-112	82-122	20	90-110	-	-	-
1,2,3,4,7,8,9-HpCDF	50	16.2	86-126	78-130	20	86-116	-	-	-
OCDD	100	19	89-127	78-130	20	79-125	-	-	-
OCDF	100	27	74-146	70-130	35	75-125	-	-	-
Surrogate Standards									
¹³ C ₁₂ -2,3,7,8-TCDD	100	37	28-134	25-130	35	82-121	40-120	25-130	40-130
¹³ C ₁₂ -2,3,7,8-TCDF	100	35	31-113	25-130	35	71-130	40-120	24-130	40-130
¹³ C ₁₂ -1,2,3,7,8-PeCDD	100	39	27-184	25-150	35	70-130	40-120	25-130	30-130
¹³ C ₁₂ -1,2,3,7,8-PeCDF	100	34	27-156	25-130	35	76-130	40-120	24-130	30-130
¹³ C ₁₂ -2,3,4,7,8-PeCDF	100	38	16-279	25-130	35	77-130	40-120	21-130	
¹³ C ₁₂ -1,2,3,4,7,8-HxCDD	100	41	29-147	25-130	35	85-117	40-120	32-130	
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	100	38	34-122	25-130	35	85-118	40-120	28-130	30-130
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	100	43	27-152	25-130	35	76-130	40-120	26-130	30-130
¹³ C ₁₂ -1,2,3,6,7,8-HxCDF	100	35	30-122	25-130	35	70-130	40-120	26-123	
¹³ C ₁₂ -1,2,3,7,8,9-HxCDF	100	40	24-157	25-130	35	74-130	40-120	29-130	
¹³ C ₁₂ -2,3,4,6,7,8-HxCDF	100	37	29-136	25-130	35	73-130	40-120	28-130	

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¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	100	35	34-129	26-130	35	72-130	40-120	23-130	30-130
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	100	41	32-110	25-130	35	78-129	40-120	28-130	30-130
¹³ C ₁₂ -1,2,3,4,7,8,9-HpCDF	100	40	28-141	25-130	35	77-129	40-120	26-130	
¹³ C ₁₂ -OCDD	200	47.5	20.5-138	25-130	35	70-130	25-120	17-130	30-130
Cleanup Standard									
³⁷ Cl ₄ -2,3,7,8-TCDD	10	36	39-154	31-130	35	79-127	40-120	35-130	

* For comparability with EPA 1613B the precision specification for IPR is stated as %SD (=standard deviation relative to the fortification level,)

QC Specification Table: QC Samples, Instrumental Analysis, and Analyte Quantification

QC Parameter	Specification
Analysis Duplicate	Must agree to within $\pm 20\%$ of the mean (applicable to concentrations > 10 times the DL) ¹
Procedural Blank	Blood: TCDD/F < 0.2 pg/sample, PeCDD/F < 0.5 pg/sample, HxCDD/F and HpCDD/F < 1.0 pg/ sample, OCDD/F < 5 pg/sample. Other Matrices: TCDD/F < 0.5 pg/sample, PeCDD/F, HxCDD/F, HpCDD/F < 1.0 pg/sample, OCDD/F < 5 pg/sample. Higher levels acceptable where all sample concentrations are $> 10X$ the blank concentrations.
Detection Limit	SDL Requirements Blood: Tetra-penta-CDD/F 0.2 pg/sample Hexa-octa-CDD/F 0.5 pg/sample Other Matrices: 1 pg/sample
Instrument Carry over and Background: Toluene Blank	A. 1 st toluene blank following Cal Ver must have < 0.6 pg TCDD and < 25 pg OCDD ² . B. 2 nd toluene blank following Cal Ver must have < 0.2 pg TCDD/F, < 0.8 pg Pe-HpCDD/F, and < 5.0 pg OCDD ² . Blood Extract Analysis: as many toluene blanks as necessary are run to achieve an instrument blank level of < 0.1 pg TCDD/F, < 0.3 pg PeCDD/F, < 0.5 pg HxCDD/F, < 0.5 pg HpCDD/F and < 3.5 pg OCDD.
Samples	$< 10\%$ contribution from preceding sample (based on observed instrument carryover rate).
Analyte/Surrogate Ratios	Response must be within the calibrated range of the instrument. Data may be taken from more than one chromatogram to get the responses in the calibrated range.
Ion Ratios	Must be within $\pm 15\%$ of theoretical. For 1613B applications only an alternate acceptance criteria of within $\pm 10\%$ of the ratio in the midpoint calibration (CS3) or calibration verification (Cal Ver), whichever is most recent., may be applied.
Sensitivity	S:N $\geq 10:1$ for all compounds for 0.1 pg/ μ L (CS-0.2) plus, for bloods, S:N $\geq 3:1$ for 0.025 pg/ μ L 2,3,7,8-TCDD.

¹ Duplicate criterion is a guideline; final assessment depends upon sample characteristics, overall batch QC and on-going lab performance.

² Instrument background specifications are calculated from spiking labelled standard into the toluene blank and expressed as pg in a 20 μ L extract.

REFERENCES:

1. United States Environmental Protection Agency *Method 1613, Revision B. Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS.*
2. USEPA *Method 8290, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Revision 0, September 1994.*
3. USEPA *Method 8290A, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Revision 1, January 1998.*
4. Environment Canada: *Reference Method for the Determination of Polychlorinated Dibenzopara-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Pulp and Paper Mill Effluents*, Report EPS 1/RM/19 Feb 1992.
5. USEPA *Method DLM02.1, Statement of Work (SOW) for Analysis of Chlorinated Dibenzop-dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs)*, January 2009.

APPENDIX A

SUMMARY OF MODIFICATIONS TO EPA METHOD 1613B

The following sections of EPA Method 1613B have been modified as described below.

Section 2.1.2

Non-aqueous liquid from multiphase samples is combined with the solid phase and extracted by Dean Stark soxhlet.

Section 7.2.1

Anhydrous sodium sulphate (Na_2SO_4) is baked overnight prior to use. There is no solvent rinse with dichloromethane.

Section 7.10

The concentration of the labelled compound spiking solution is 100 ng/mL (except for OCDD which is 200 ng/mL) and the sample spiking volume is 20 μL . The resulting concentrations in the final extracts are as specified in the method.

Section 7.11

The concentration of the clean-up standard spiking solution is 10 ng/mL and the sample spiking volume is 20 μL . The resulting concentration in the final extracts are as specified in the method.

Sections 7.13, 14.0, 15.0

An additional lower level calibration solution, 0.2 times the concentration of CS1, is prepared and may be included in the initial calibration series so that initial calibration is based on a six-point series.

Section 7.14

The concentration of the PAR spiking solutions is 0.2/1.0/2.0 ng/mL for tetra/penta, hexa, hepta, hexa/octas respectively and the spiking volume is 1 mL. The resulting final concentration in the extracts are as specified in the method.

Section 9.3.3

Table 7 (EPA 1613B) specifications for the percent recovery of surrogate standards in samples that are higher than 130% have been lowered to 130%, as presented in table "QC Specification Table: Authentic and Surrogate Standard Recoveries, CAL/VER, IPR, OPR and Samples" of this document.

Section 11.5

Aqueous samples containing $>1\%$ visible solids are prepared and extracted using the same procedure as samples containing $\leq 1\%$ visible solids. This involves extracting the solids by soxhlet and the filtrate by separatory funnel extraction and combining the extract from the two phases.

Section 12.0

Samples with sufficiently low moisture content are mixed with Na_2SO_4 and extracted using regular soxhlet apparatus in 80:20 toluene:acetone.

Section 12.3.1 – 12.3.5

Silica or quartz sand is not pre-extracted in the Dean Stark apparatus. Silica is baked the lab. Quartz sand is proofed prior to use. Sand is mixed with the sample in a beaker and then loaded into the soxhlet thimble.

Section 12.3.9.1.1

Sample extracts are reduced to approximately 1mL after extraction, not 5 mL.

Section 12.4

The equilibration time for the sodium sulphate drying step is sufficient to produce a dry, free-flowing powder (minimum 30 minutes). This may be less than the 12-hour minimum specified in EPA 1613B.

Section 12.5.1

Samples are spiked with cleanup standard right after extraction and before reduction; not spiked into the separatory funnels containing the extracts prior to the acid/base wash.

Section 12.5.3

Ultra-pure water is used to rinse the extract between base and acid washes, not NaCl solution.

Section 12.6.1.1

Rotary evaporator baths are maintained at 35°C. Mimic proofs are collected instead of collecting proofs each day and archiving.

Section 12.7.3

Water baths are not used with the nitrogen blowdown apparatus.

Section 12.7.4

Solvent exchange is dependent on the type of solvent present: if toluene is present the extract is reduced to 50 µL and topped up to 1 mL with hexane; if dichloromethane is present the extract is reduced to 300 µL and topped up to 1 mL with hexane.

Section 12.7.7

Sample extracts are concentrated in a microvial using nitrogen to near dryness before adding the recovery standard.

Section 13.0

Extracts may be cleaned up on silica, alumina and carbon chromatographic columns using a Fluid Management System (FMS) automated cleanup system.

Section 13.7

Gravimetric lipid analysis is carried out on two subsamples of the extract, representing 2/15ths of the extract. A correction factor is applied to the surrogate recovery standards.

Sections 14.0, 15.0, 16.0, Table 8, Table 9

M/Z channels 354/356 and 366/368 are used to confirm and quantify the native and surrogate penta-substituted dioxins, respectively; this change from the method's specification is made in the instrument method in order to avoid a persistent interference in the 356/358 and 368/370 M/Z channels. The theoretical ratio for the P5CDD M/M+2 ions is 0.61; therefore, the acceptance range is 0.52 - 0.70.

Section 14.2

Toluene instead of nonane is used to bring extracts back to volume.

Section 15.3.5

Table 6 (EPA 1613B) specifications for CAL-VER solution concentrations outside the 70-130% range have been revised to be 70-130%, as presented in table "QC Specification Table: Authentic and Surrogate Standard Recoveries, CAL/VER, IPR, OPR and Samples" of this document.

Section 15.3.3

Table 6 (EPA 1613B) specifications for OPR concentrations outside the 70-130% range have been revised to be 70-130%, as presented in table "QC Specification Table: Authentic and Surrogate Standard Recoveries, CAL/VER, IPR, OPR and Samples" of this document.

Section 17.0

Conci - the concentrations of target analytes, and the labelled compound concentrations and recoveries, are calculated using the equations below. These procedures are equivalent to those described in the method but are more direct.

$$Conc = \frac{A_i}{A_{si}} \times \frac{M_{si}}{RRF_{i,si}} \times \frac{1}{M_x}$$

where A_i = summed areas of the primary and secondary m/z's for the analyte peak of interest (compound i)

A_{si} = summed areas of the primary and secondary m/z's for the labelled surrogate peak used to quantify i)

M_x = mass of sample taken for analysis

M_{si} = mass of labelled surrogate (compound si) added to sample as calculated by the concentration of standard spiked (pg/mL) multiplied by the volume spiked (mL)

$RRF_{i,si}$ = mean relative response factor of i to si from the five-point calibration range and defined individually as:

$$\frac{A_i}{A_{si}} \times \frac{M_{si}}{M_i}$$

Calculation of Surrogate Standard Concentrations and Percent Recoveries:

Concentrations of surrogate standards are calculated using the following equation:

$$Conc_{si} = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}}$$

and, the percent recoveries of the surrogate standards are calculated using the following equation:

$$\%Recovery = \frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{RRF_{si,rs}} \times \frac{1}{M_{si}} \times 100$$

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where A_{rs} and A_{si} are the summed peak areas (from the primary and secondary m/z channels) of recovery standard and labelled surrogate added to the sample;
 M_{rs} and M_{si} are the masses of recovery standard and labelled surrogate added to the sample, and;
 $RRF_{si,rs}$ is the mean relative response factor of the labelled surrogate to the recovery standard as determined by the five-point calibration range and defined individually as:

$$\frac{A_{si}}{A_{rs}} \times \frac{M_{rs}}{M_{si}}$$

Section 17.5

Extracts may be diluted with solvent and re-analyzed by GC/MS to bring the instrumental response to within the linear range of the instrument. Typically, no additional recovery (internal) standard is added. For very high-level samples where a smaller sample aliquot may not be representative, extracts may be diluted and respiked with labelled quantification standards and re-analyzed by GC/MS to bring the instrumental response analytes within range. Final results are recovery corrected using the mean recovery of labelled quantification standards.

APPENDIX B

SUMMARY OF MODIFICATIONS TO EPA METHOD 8290

The following modifications apply to EPA Method 8290.

1. A sample hold time of 30 days from time of sample collection is recommended. Extract hold time, stored at -10°C , is 45 days.
2. Solid samples are dried with sodium sulphate and Soxhlet extracted using 80:20 toluene:acetone. Upon client request, optional extraction using Soxhlet Dean-Stark and toluene is available.
3. The same surrogate, recovery, authentic spike and calibration solutions that are used for EPA method 1613B (described in table "Concentration of PCDD/PCDF Calibration Solutions" of this document) are used to perform EPA Method 8290.
4. The quantification is performed according to EPA Method 1613B, using an expanded suite of surrogate standards as summarized in Table "Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans" of this document. On client request, quantification may be performed using the smaller suite of surrogate standards described in EPA 8290 (refer to table "Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans by EPA 8290" below).
5. Sample Specific Estimated Detection Limits (EDL) are reported as Sample Specific Detection Limits (SDL), calculated as described in Section "Reporting Limits" of this document.
6. Modifications made to EPA 1613B, as described in Appendix A of this document, are applicable.
7. The QC specifications in the table "QC Criteria for PCDD/F Analysis by EPA 8290" (see below) of this document are used for evaluating data.

QC Criteria for PCDD/F Analysis by EPA 8290

Initial Calibration	Native analytes: $\pm 20\%$ RSD for mean RRF Labelled Compounds: $\pm 30\%$ RSD for mean RRF
CAL-VER	Native Analytes: RRF must be $\pm 20\%$ of mean RRF from ICAL Labelled Compounds: RRF must be $\pm 30\%$ of mean RRF from ICAL
Sample Surrogate Recovery	40-135% (lower or higher recoveries for the procedural blank may be accepted based on analyst professional judgement.)
Spiked Reference Sample	In house specification: 70%-130% of the expected value for all targets except 1,2,3,7,8,9-HxCDF, which is 60%-140%. Professional judgement may be applied in consideration of overall QC data, including MS/MSD to determine acceptability.
Analysis Duplicate	Must agree to within 25% RPD
MS/MSD	Must agree to within 20% RPD

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Analyte Ions Monitored, Surrogates Used and RRF Determination for Dioxins/Furans by EPA 8290

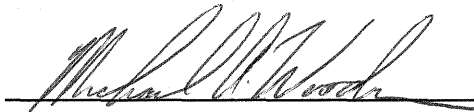
Analytes	Quantification Ion (m/z)	Confirmation Ion (m/z)	Surrogate	RRF Determined From
2,3,7,8-TCDD	320	322	¹³ C ₁₂ -2,3,7,8-TCDD	2,3,7,8-TCDD
1,2,3,7,8-PeCDD	354	356	¹³ C ₁₂ -1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	390	392	¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD	390	392	¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	390	392	¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD	424	426	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD
OCDD	458	460	¹³ C ₁₂ -OCDD	OCDD
2,3,7,8-TCDF	304	306	¹³ C ₁₂ -2,3,7,8-TCDF	2,3,7,8-TCDF
1,2,3,7,8-PeCDF	340	342	¹³ C ₁₂ -1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	340	342	¹³ C ₁₂ -1,2,3,7,8-PeCDF	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDF	374	376	¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF	374	376	¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	374	376	¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	2,3,4,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	374	376	¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	1,2,3,7,8,9-HxCDF
1,2,3,4,6,7,8-HpCDF	410	412	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	410	412	¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF
OCDF	442	444	¹³ C ₁₂ -OCDD	OCDF
Labelled Surrogate Stds	Quantification Ion (m/z)	Confirmation Ion (m/z)	Recovery Calculated Using	
¹³ C ₁₂ -2,3,7,8-TCDF	316	318	¹³ C ₁₂ -1,2,3,4-TCDD	
¹³ C ₁₂ -2,3,7,8-TCDD	332	334	¹³ C ₁₂ -1,2,3,4-TCDD	
¹³ C ₁₂ -1,2,3,7,8-PeCDF	352	354	¹³ C ₁₂ -1,2,3,4-TCDD	
¹³ C ₁₂ -1,2,3,7,8-PeCDD	366	368	¹³ C ₁₂ -1,2,3,4-TCDD	
¹³ C ₁₂ -1,2,3,4,7,8-HxCDF	384	386	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -1,2,3,6,7,8-HxCDD	402	404	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -1,2,3,4,6,7,8-OCDF	418	420	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -1,2,3,4,6,7,8-HpCDF	436	438	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
¹³ C ₁₂ -OCDD	470	472	¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	
Labelled Recovery Stds				
¹³ C ₁₂ -1,2,3,4-TCDD	332	334		
¹³ C ₁₂ -1,2,3,7,8,9-HxCDD	402	404		


Appendix N
Laboratory SOPs


Shealy SOP
S-IM-021, Revision 2

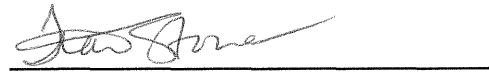
Metals
By EPA 6020

SHEALY ENVIRONMENTAL SERVICES, INC.
STANDARD OPERATING PROCEDURE
INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY
ANALYSIS METHOD 6020A


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1. SCOPE AND APPLICATION

- 1.1 This procedure describes multi-elemental analysis by inductively coupled plasma / mass spectrometry (ICP-MS) using SW-846 protocols as described in EPA Method 6020A . The source method lists seventeen elements approved for analysis by ICP-MS. Additional elements have been approved by EPA Region IV as analyzed under Method 6020A provided that the method performance criteria presented in Section 13 are met. Refer to Table VII for the full target analyte list.
- 1.2 This procedure also describes the requirements for performing analysis of ground waters, surface waters, soils, sludges, sediments, and other solid wastes.
- 1.3 ICP-MS analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrix and instrument used. For instance, in comparison to conventional ICP techniques, which cannot achieve graphite furnace atomic absorption spectroscopy (GFAAS) detection limits, the ICP-MS can achieve detection levels comparable to or better than those determined using the GFAAS technique.
- 1.4 The procedure is applicable to the analysis of waters, wastes, soils, sludges, sediments, and other solid wastes. No digestion is required prior to analysis for dissolved elements in water samples, and the samples must be filtered and preserved prior to analysis. Preliminary acid digestion is required for groundwater, and other aqueous samples, for which total (acid-leachable) elements are requested.
- 1.5 This document accurately reflects current laboratory standard operating procedures (SOP) as of the date above. All SOPs are maintained and updated as necessary.

2. SUMMARY OF METHOD

- 2.1 Aqueous samples, digestates, or leachates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into a Radio-Frequency (RF) plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrupole mass spectrometer capable of providing a resolution better than or equal to 0.9 amu peak width at 10 % of the peak height. For analysis the resolution requirement is 1.0 amu at 5 % peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier. Interference must be assessed and valid corrections applied, or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and the constituents of the sample matrix. Recommended elemental equations which correct for many of these interferences are listed in Table I. Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices.

- 2.2 Refer to S-IM-008, S-IM-009 or S-IM-015 SOPs for details on sample preparation.

3. DEFINITIONS

- 3.1 Dissolved Metals – Those elements that pass through a 0.45 µm membrane. (Sample is acidified after filtration.)
- 3.2 Suspended Metals – Those elements that are retained by a 0.45 µm membrane.
- 3.3 Total Metals – The concentration determined on an unfiltered sample following vigorous digestion.
- 3.4 Total Recoverable Metals – The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.
- 3.5 Sensitivity - The slope of the analytical curve (i.e. the functional relationship between raw instrument signal and the concentration).
- 3.6 Tuning Solution - This is a multi-element solution containing analytes that are representative of the entire mass range capable of being scanned by the instrument. It is used to optimize the sensitivity of the instrument and to verify the mass resolution meets method criteria.
- 3.7 Quality Control Standard (QCS) = Initial Calibration Verification (ICV) - A multi-element standard of known concentrations prepared to verify instrument calibration. This solution must be an independent standard prepared near the mid-point of the calibration curve, and at a concentration other than that used for instrument calibration.
- 3.8 Instrument Performance Check (IPC) = Continuing Calibration Verification (CCV). - A multi-element standard of known concentrations prepared to monitor and verify the instrument daily continuing performance.
- 3.9 Interference Check Standard (ICS) - A solution containing both interfering and analyte elements of known concentration that is used to verify background and interelement correction factors.
- 3.10 Laboratory Fortified Blank (LFB) = Laboratory Control Sample (LCS) - A multi-element standard of known concentrations which is carried through the entire sample preparation and analysis procedure. This solution is used to verify the accuracy of the sample preparation.
- 3.11 Reagent Blank = Method Blank - High purity water carried through the entire digestion process.

- 3.12 Calibration Blank - High purity water acidified with the same acid concentrations present in the standards and samples also referred to as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB).
- 3.13 Method Detection Limit (MDL). The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in Shealy QAMP.

4. INTERFERENCES

- 4.1 Isobaric Interferences - Isobaric interferences in the ICP-MS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software.
- 4.2 Isobaric Molecular and Doubly Charged Ion Interferences - Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. Table II lists isobaric interferences that might possibly affect required analytes. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied and the data flagged to indicate the presence of interferences.
- 4.3 Physical Interferences - Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.
 - 4.3.1 Internal standards should be added at a level to give approximately 100,000 – 1,000,000 counts of raw signal intensity. The mass of the internal standard should ideally be within 20 amu of the mass of the measured analyte.
 - 4.3.2 The intensities of all internal standards must be monitored. If the intensity of any internal standard in a sample falls below 70 % of the intensity of the internal standard in the initial calibration blank, then a matrix effect is suspected. If the count per second (cps) falls below 70 %, corrective action must be taken. First, make sure the instrument has not drifted by observing the internal standard intensities in the blank. If low internal standard intensities are also seen in the blank, terminate the analysis, correct the problem, recalibrate, verify calibration, and reanalyze the samples. If drift has not occurred, dilute the sample fivefold (5x) and reanalyze. More dilutions may be necessary if the 5x dilution does not eliminate the problem.
 - 4.3.3 Memory effects are dependent on the relative concentration differences between samples and/or standards that are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

- 4.3.4 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

5. SAFETY

- 5.1 Procedures shall be carried out in a manner that protects the health and safety of all Shealy personnel.
- 5.2 As stated in the Shealy Comprehensive Chemical Hygiene, Safety, and Hazard Communication Plan (P-HS-003), eye protection that satisfies ANSI Z87.1, laboratory coat, and at least latex gloves must be worn while samples, standards, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.
- 5.3 The health and safety hazards of many of the chemicals used in the procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.
- 5.3.1 The following materials are known to be **corrosive**: sulfuric acid, hydrochloric acid, and nitric acid. (NOTE: sulfuric acid and hydrofluoric acids are used in cleaning the ICP torch and hydrofluoric acid is also commonly used in air toxics preparations.)
- 5.3.2 The following materials are known to be **oxidizing agents**: nitric acid and hydrogen peroxide.
- 5.3.3 The plasma emits strong UV light and is harmful to vision.
- **Note: Avoid looking directly at the plasma.**
- 5.3.4 The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.
- 5.4 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.
- 5.5 The preparation of standards and reagents will be conducted in a fume hood or well-ventilated area.

- 5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of a Shealy employee. The situation must be reported immediately to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

- 6.1 A Thermo Elemental X-5 Inductively Coupled Plasma Mass Spectrometer capable of providing resolution, less than or equal to 0.9 amu at 10 % peak height from 6-253 amu and 1.0 amu at 5 % peak height from 6-253 amu with a data system that allows corrections for isobaric interferences and the application of the internal standard technique.
- 6.2 Radio Frequency Generator.
- 6.3 Argon gas supply, High purity grade 99.99 % or better.
- 6.4 Coolflow or appropriate water-cooling device.
- 6.5 Peristaltic Pump.
- 6.6 Calibrated automatic pipets with appropriate pipet tips or class A volumetric pipets.
- 6.7 Class A volumetric flasks.
- 6.8 Autosampler with autosampler tubes.

- **Note: All stored reagents and standards are labeled with the following information:**

1. **Name of standard or solution**
2. **Concentration**
3. **Analyst's Initials**
4. **Prep date**
5. **Expiration date**
6. **Tracking number**
7. **Warning label of any hazards and/or concentration of acid or base**

7. REAGENTS AND STANDARDS

- 7.1 Refer to S-QA-007 for all glassware cleaning procedures before using any glassware.
- 7.2 Intermediate standards are purchased as custom multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon or unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the

expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solution may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

- 7.3 Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in the same acid matrix.
- 7.4 Refer to Tables VIII, IX, X, and XI for details regarding the working standard concentrations for calibration, calibration verification, interference correction, and spiking solutions.
- 7.5 The tuning solution is purchased as custom Shealy multi-element mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or unused polyethylene or polypropylene bottles. The solution must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to two years.
- 7.6 Concentrated nitric acid (HNO_3), trace metal grade or better.
- 7.7 Concentrated hydrochloric acid (HCl), trace metal grade or better.
- 7.8 Reagent water must be produced by a Continental DI water system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.
- 7.9 Rinse Solution (or, rinse blank): Carefully dilute 100 mL of concentrated HNO_3 and 20 mL of concentrated HCl to 2.0 L with reagent water.
- 7.10 Internal Standard Mix Stock – Purchase an Internal Standard Mix containing Li and Sc at 100 mg/l and Ga, Y, In, Tb, and Bi at 20 mg/l.
- 7.11 Internal Standard Mix – Dilute 2 ml of Internal Standard Mix Stock (7.10) to 1000 ml in 1 % HNO_3 .

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1 Sample holding times for metals are six months from time of collection to the time of analysis.
- 8.2 Aqueous samples are preserved with nitric acid to a pH of < 2 and may be stored in either plastic or glass. If boron or silica is to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3 Drinking water samples

- 8.3.1 Dissolved samples must be filtered through a 0.45 μm pore diameter membrane. Filter at the time of collection or as soon thereafter as practically possible. Acidify the filtrate with 1:1 nitric acid immediately following filtration to $\text{pH} < 2$.
- 8.3.2 For total recoverable elements, preservation may be done at time of collection, or, upon receipt at the laboratory. The time allowed for traveling to the laboratory cannot exceed two weeks from sample date. Following acidification, the sample should be mixed, held for 24 hours, and then verified to be $\text{pH} < 2$ just before analysis or prep (if prep required). If pH is not < 2 , add more acid and hold for 24 more hours until verified to be $\text{pH} < 2$.

9. QUALITY CONTROL

9.1 Initial Demonstration of Capability:

- 9.1.1 The initial demonstration of capability (IDOC) and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.2 Instrument Detection Limit (IDL) and Lower Limit of Quantitation Check (LLQC)

- 9.2.1 Instrument Detection Limits (IDL)
Method 6020A: Calculate the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. IDLs must be determined at least every three months and kept with the instrument logbook.
- 9.2.2 Lower limit of quantitation check sample (LLQC) - The lower limit of quantitation check should be analyzed after establishing the reporting limits (yearly). Ideally, this check sample is carried through the entire preparation and analytical procedure. The check sample should recover within 30 % of the true value. This check is used to establish and confirm the lowest quantitation limit.

- 9.3 Linear Dynamic Range Verification (LDR) –The linear range must be determined at least every six months for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample. The standards used to define the linear range limit must be analyzed during a routine analytical run. For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across

the estimated range. One standard should be near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10 % different from the true value. If the instrument is adjusted in any way that may affect the LR's, new dynamic ranges must be determined. The LR data must be documented and kept on file.

- 9.4 Laboratory Reagent Blank (LRB) = Method Blank (MB) – One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.
- 9.4.1 For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank should not be higher than the highest of either:
- 9.4.1.1 The practical quantitation limit (PQL), or RL
 - 9.4.1.2 Ten percent of the regulatory limit, or
 - 9.4.1.3 10 % of the sample concentration for each analyte
 - 9.4.1.4 If the method blank does not meet the above criteria, rerun once and if still fail, then the 20 samples in the batch associated with that MB must be redigested and reanalyzed. If the samples are all below the reporting limit, then the data may be used even if the method blank is contaminated.
- 9.4.2 If the above criteria are not met and reanalysis is not possible due to limited sample volume, then the sample data must be qualified. Such action must result in the completion of an NCM. Refer to Procedural Variations (11.19, 11.19.1) for more detail.
- 9.5 Laboratory Fortified Blank (LFB) = Laboratory Control Sample (LCS) – One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table VIII (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.
- 9.5.1 If any analyte is outside established control limits, the system is out of control and corrective action must be taken. For method 6020A, a control limit of 80 – 120 % recovery must be applied. If the LCS is not acceptable, rerun once and if still unacceptable, all samples should be redigested and reanalyzed.

9.5.2 For metals samples, which have not been digested, an undigested LCS is used.

- 9.6 Matrix Spike, Unspiked Duplicate (MS/DUP), or Matrix Spike/Matrix Spike Duplicate (MS/MD) also known as the Laboratory Fortified Matrix (LFM) – At least one MS/DUP or MS/MSD should be included per sample batch of 20 or less. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MD) is a second aliquot of the same sample (spike identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MD. The MS/DUP or MS/MD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/DUP or MS/MD analysis. Spiking levels are provided in Table VIII (Appendix A). For method, 6020A, control limits of 75 % - 125 % recovery and 20 % RPD acceptance criteria must be applied to the MS/MD. If the control limits are met, then interference tests (post digestion spike and /or dilution test) should be done.
- 9.7 Post digestion spike (PDS) - If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD were prepared should be spike with a post digestion spike. Another sample can be used as an alternative if the original sample was consumed. An analyte spike is added to a portion of the sample or its dilution, and should recover to within 80-120 %. If the spike fails, then the dilution test should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.
- 9.8 Dilution Test- A dilution test is performed to determine if significant physical or chemical interferences exists due to the sample matrix. If the analyte concentration is sufficiently high (minimally 10x the lower limit of quantitation after dilution) an analysis of a 5x dilution should agree within 10 % of the original concentration. If not, then a chemical or physical interference is suspected.
- 9.9 Initial Calibration Verification (ICV/LLICV) – Calibration accuracy is verified by analyzing a second source standard (ICV) at or near the mid-range of the calibration curve. The ICV result must fall within 10 % of the true value. In addition, a low-level initial calibration standard (LLICV) should be prepared, using the same source as the calibration standards. The LLICV must recover within 30 % of its true value.
- 9.10 Continuing Calibration Verification (LLCCV/CCV/CCB) – Calibration accuracy is monitored throughout the analytical run by the analysis of a known standard after every 10 samples. The CCV is a mid-range standard made from a dilution of the calibration standard.
- 9.10.1 The CCV must be within 10 % of the expected value for samples to be reported. A CCB is analyzed immediately following the CCV. The low

level continuing calibration verification (LLCCV) should also be analyzed at the end of each analysis batch. The acceptance criteria for the LLCCV standard should be 30 % of its true value. The LLCCV analysis may be necessary after every 10 samples to minimize the number of re-runs should the LLCCV fail if only run at the end of the analysis batch. If the LLCCV/CCV fails, the analysis must be discontinued, the cause determined, the instrument recalibrated and the samples associated with the failing LLCCV or CCV reanalyzed.

9.10.2 The CCB should not contain analytes above the reporting limits. If the CCB fails, the analysis should be terminated, the cause determined, the instrument recalibrated and the samples associated with the failed CCB reanalyzed.

9.11 Interference Check Solutions (ICSA/ICSAB) - The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The interference check solutions must be analyzed at the beginning of every analytical run or once every 12 hours, whichever is more frequent. The results of solution "A" and solution "AB" should be monitored for possible interferences. The ICSA contains only interfering elements, the ICSAB contains analytes and interferences. Refer to Table XI (Appendix A) for details of ICSA and ICSAB composition. Custom multi-element ICS solutions must be used. All analytes should be spiked into the ICSAB solution, therefore, if a non-routine analyte is required then it should be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix.

9.11.1 The ICSA and ICSAB solutions must be run at the beginning of the run or once every 12 hours, whichever is more frequent.

9.11.2 Control limits of spiked analytes in the ICSA/ICSAB solution are $\pm 50\%$ of true value. Some projects may require control limits of $\pm 20\%$ of true value. Control limits of non-spiked analytes are $\pm 2x$ the practical quantitation limit or less than 10 ug/L. If the ICSA results for the non-interfering elements do not fall within $\pm 2x$ PQL or less than 10 ug/L the field sample data must be evaluated as follows:

9.11.2.1 If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.

9.11.2.2 If the affected element was not required then the sample data can be accepted.

9.11.2.3 If the interfering elements are not present in the field sample at a concentration which would result in a false positive or negative result

greater than $\pm 2x$ PQL from zero then the field sample data can be accepted.

- 9.11.2.4 If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than $\pm 2x$ PQL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.

Note: It may not be possible to obtain absolutely clean ICSA/ICSAB standards. If contamination can be confirmed by another method (ICP), acceptance criteria will be applied at that level and the data accepted

10. CALIBRATION AND STANDARDIZATION

- 10.1 Set up the instrument according to manufacturers operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning.
- 10.2 Instrument Tuning / Mass Calibration / Daily Performance.

Daily Performance – Refer to Appendix A for ICP-MS Instrument Instructions. Instrument manuals are available as needed. Verify instrument performance daily with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5 % after running the tuning solution a minimum of 4 times.

- 10.2.1 Check the mass calibration and the resolution daily.

10.2.1.1 Mass Calibration Check – The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted and verified before running samples. Refer to table V, “Tuning Solution” for the elements and the masses checked.

10.2.1.2 Mass Resolution Check - The resolution must be verified to be less than 0.75 amu full widths at 5 % peak height. If this criterion is not met, the mass resolution check must be adjusted and verified before running samples.

- 10.3 Calibrate the instrument for the analytes of interest according to manufacturer’s instructions. Routine calibration and calibration verification levels are shown in Tables IX and X. The calibration should include a blank and at least three standards for each analyte. For a linear, multi-point calibration curve, the correlation coefficient must be ≥ 0.998 . Report the average of at least three integrations for both calibration and sample analysis. A calibration must be performed daily and each time the instrument is set up.

Instrument run may be continued over periods exceeding 24 hours as long as calibration verification, interference check, and internal standard QC criteria are met.

- 10.4 Refer to Section 9 for calibration verification procedures, acceptance criteria, and corresponding corrective actions.

11. PROCEDURE

- 11.1 All dissolved samples (drinking water, groundwater, and wastewater) must be digested according to S-IM-008, S-IM-009, or S-IM-015.
- 11.2 All drinking water samples must be digested unless it can be documented that the sample meets all of the following criteria:
- 11.2.1 Visibly transparent with a turbidity measurement of <1 NTU.
- 11.3 All other samples (groundwater and wastewater) are digested according to S-IM-008,
- 11.4 Sample Preparation
- 11.4.1 Preliminary acid digestion is required for groundwater and aqueous samples, for which total (acid-leachable) elements are requested. Refer to the table below for the appropriate prep methods.

ICP-MS Matrix	Prep Methods for CWA	Analysis Methods for CWA	Approved Prep Methods for SDWA	Approved Analysis Methods for SDWA	Approved Prep Methods for RCRA	Approved Analysis Methods for RCRA
Drinking water (NTU<1)			No prep required	200.8		
All other Aqueous	200.2	200.8	200.8	200.8	3005A	6020A

Sample Analysis

- 11.4.2 Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.
- 11.4.3 Masses which would affect the data quality must be monitored during the analytical run to determine the potential effects of matrix on a given element.

11.4.4 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte or specific isotope of interest. No analyte may be reported from an analysis of a diluted sample in which the analyte concentration is less than 5 times the IDL (the sample should be diluted to the approximate midrange of the analytical curve), unless the dilution is for internal standard recoveries. The only other exception is below:

11.4.4.1 If the sample contains extreme amounts of target or non-target elements and has been analyzed at the least dilution possible without damaging the instrument, then any analytes that remain at a concentration less than 5 times the IDL may be reported.

11.4.5 The analytical run sequence should be performed as follows to meet all quality control criteria:

- 1 Warm-up
- 2 Verify instrument performance (Tune)
- 3 Calibration blank
- 4 Calibration standards
- 5 LLICV
- 6 ICV
- 7 ICB
- 8 ICSA
- 9 ICSAB
- 10 LLCCV/CCV/CCB
- 11 10 samples (Batch QC are included in sample count)
- 12 LLCCV/CCV/IPC
- 13 CCB
- 14 Repeat sequence of up to 10 samples between LLCCV/CCV/CCB pairs as required to complete the sequence.
- 15 ICSA/ICSAB should be analyzed at least once every 12 hours

11.5 Analytical Documentation

11.5.1 All standards are logged into a department standard logbook. All standards are assigned a unique number for identification.

11.5.2 Documentation such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs is available for each data file.

11.5.3 Sample results and associated QC are entered into the LIMS after final technical review.

11.6 Procedural Variations – This Section applies to all samples except South Carolina compliance samples. One time procedural variations are allowed, only if deemed

necessary in the professional judgment and supervision of a knowledgeable analyst, to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in analytical procedure must be approved by a technical director, the QA Officer, or the client, and must be fully documented (flagged and/or narrated) on the final report. The analyst must use an NCM to notify the appropriate parties and to document the variance. The project manager uses the information on the NCM to notify the client and flag/narrate the final report accordingly. A copy of the NCM is kept with the raw data and the original is filed with the final report.

- 11.6.1 For South Carolina compliance samples, all procedures outlined in this SOP must be followed without exception. In the event that a deviation from this SOP cannot be avoided (i.e., demonstrated and uncorrectable matrix interference, non-compatible matrix, insufficient sample amount due to client or laboratory error) it is imperative that an NCM is completed that clearly documents the anomaly. This anomaly must be communicated to the client such that corrective action activity including sample recollection can be performed. Based upon the type and severity of anomaly, the results may not be appropriate for compliance reporting. Discussions between the client, the appropriate regulatory authority, and Shealy will be necessary to resolve certain anomalies. In any case, it is essential that any anomaly be documented on an NCM. The project manager uses the information on the NCM to notify the client and flag/narrate the final report accordingly.

12 DATA ANALYSIS AND CALCULATIONS

- 12.1 Sample results should be reported with up to three significant figures.

- 12.2 Appropriate factors must be applied to sample values if dilutions are performed.

- 12.3 ICV or CCV Percent Recovery:

- 12.4.1 LCS Percent Recovery:

Where:

X = observed concentration

t = spike concentration

- 12.5 MS or MD Percent Recovery:

Where:

X = observed concentration of un-spiked sample

X_S = observed concentration of spike sample

t = concentration of added spike

- 12.6 Relative Percent Difference between MS and MD:

Where:

X_1 = the first detected concentration

12.7 The final concentration for a digested aqueous sample is calculated as follows:

12.8 The dilution test percent difference for each component is calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

Where:

I = Sample result

S = Dilution test result

13. METHOD PERFORMANCE

13.1 Method Detection Limit – Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in Shealy QAMP.

13.2 Initial Demonstration – Each laboratory must make an initial demonstration of capability for each individual method. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equal to the LCS concentration.

13.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria for the corresponding analyte in the LCS.

13.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3 Non-standard analytes – For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration

required is analysis of an extracted standard at the reporting limit and a single point calibration.

- 13.4 Training Qualification – The team leader has the responsibility of ensuring that this procedure is being performed by an employee who has been properly trained and has the required experience.
- 13.5 Refer to Tables VII in Appendix A for the list of Method 6020A analytes as well as additional analytes that may be analyzed using this SOP.

13.6 Method performance is determined by the analysis of MS and MSD as well as method blanks and laboratory control samples. The MS or MD should fall within 75 - 125 % and the MS/MD should compare within 20 % RPD. These criteria apply to analyte concentrations greater than or equal to 10x IDL. Method blanks must meet the criteria specified in section 9. The laboratory control samples should recover within 20 % of the true value.

14. POLLUTION PREVENTION

- 14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

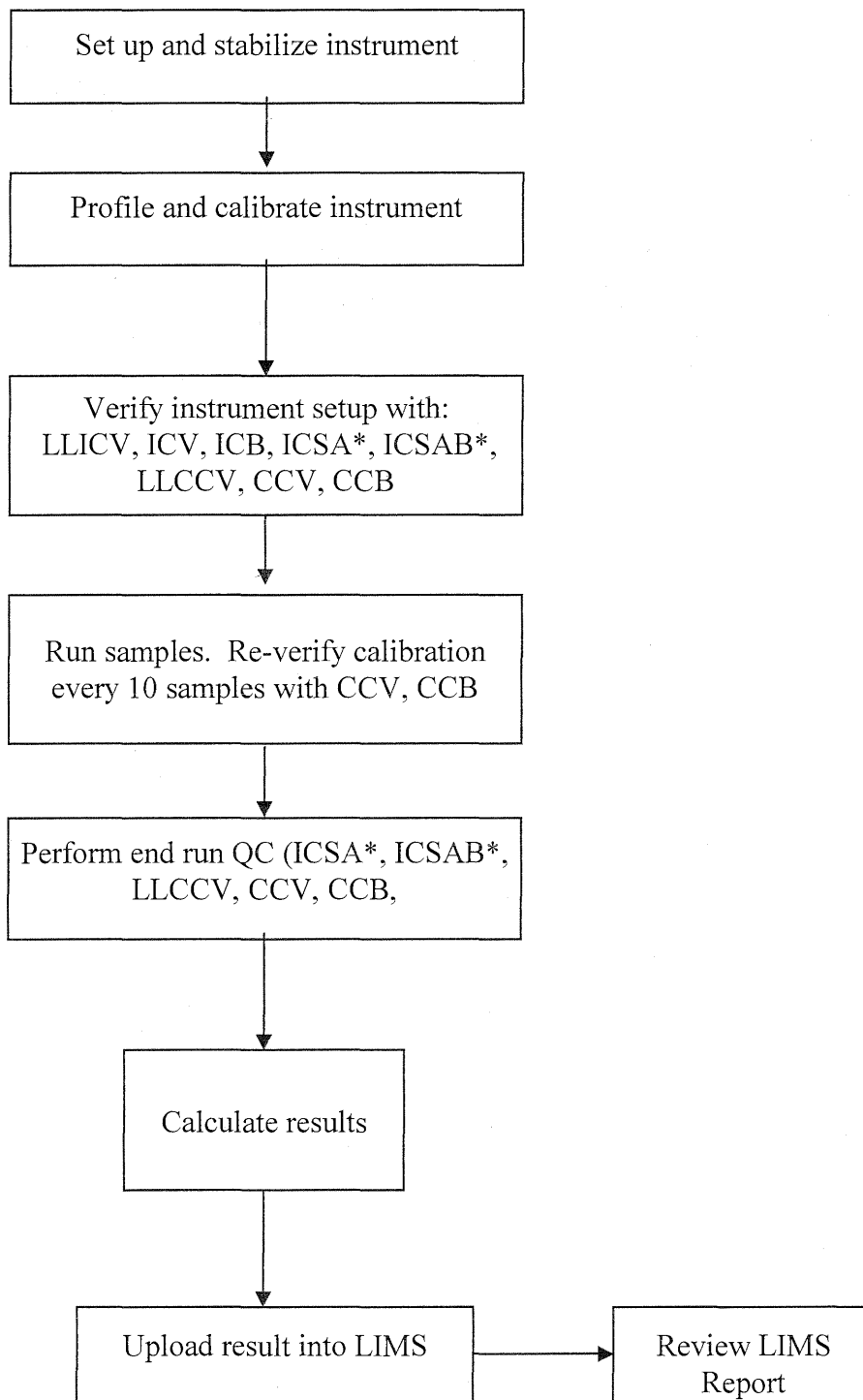
- 15.1 Waste generated in this procedure must be segregated and disposed according to the Shealy Waste Management Plan (P-HS-001). The Safety Officer should be contacted if additional information is required.

16. REFERENCES

- 16.1 40 CFR Part 136, Appendix B, Determination of Method Detection Limits.
- 16.2 Test Methods For Evaluating Solid Waste, EPA SW-846, , Method 6020A: “Inductively Coupled Argon Plasma - Mass Spectrometry”, Revision 1, February 2007
- 16.3 Environmental Monitoring Systems Laboratory, EPA Method 200.8, “Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry”, Revision 5.4, EMMC Version.
- 16.4 Shealy Quality Assurance Management Plan (QAMP), Q-QA-001
- 16.5 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.1, April 2009.

17. MISCELLANEOUS

Analysis Flow Diagram



* 6020A only

APPENDIX A TABLES

TABLE I: Recommended Elemental Interference Equations

Element	Interferant	Mathematical Equation
Ni	Fe	$58\text{Ni} = 58\text{M} - 0.0040 \cdot 56\text{Fe}$
Zn	Ni	$64\text{Zn} = 64\text{M} - 0.0440 \cdot 60\text{Ni}$
Se	Kr	$82\text{Se} = 82\text{M} - 1.0010 \cdot 83\text{Kr}$
Cd	Sn	$114\text{Cd} = 114\text{M} - 0.0270 \cdot 118\text{Sn}$
In	Sn	$115\text{In} = 115\text{M} - 0.0140 \cdot 118\text{Sn}$
Sb	Te	$123\text{Sb} = 123\text{M} - 0.1240 \cdot 125\text{Te}$
Ba	Ce	$138\text{Ba} = 138\text{M} - 0.0030 \cdot 140\text{Ce}$

M = Total ion count rate at the specified mass

TABLE II: Isobaric Molecular-Ion Interferences, Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
¹²¹ Sb	PdO		AgN			AgC	
¹²³ Sb	AgO		AgN	SrCl	ZrS	CdC	
⁷⁵ As	CoO	NiOH	NiN	ArCl	CaS	CuC	
¹³⁸ Ba	SnO	SbOH					
¹³⁷ Ba	SbO	SnOH		MoCl			
¹³⁶ Ba	SnO	SnOH				SnC	
¹³⁵ Ba	SnO	SnOH		MoCl			
¹³⁴ Ba	SnO	SnOH	SnN	MoCl		SnC	
¹³² Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
¹³⁰ Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
⁹ Be							
¹¹⁴ Cd	MoO	MoOH	MoN	SeCl	SeS		
¹¹² Cd	MoO, ZrO	MoOH	MoN	AsCl, SeCl	SeS	MoC	
¹¹¹ Cd	MoO	MoOH	MoN	GeCl			
¹¹⁰ Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
¹¹³ Cd	MoO	MoOH		SeCl, AsCl			
¹¹⁶ Cd	MoO						
¹⁰⁶ Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
¹⁰⁸ Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
⁵² Cr	ArO	ClOH				ArC	
⁵³ Cr	ClO	ArOH	KN	NCl, OCl		KC	
⁵⁰ Cr	SO		ArN		SO	ArC	Mo ⁺⁺
⁵⁴ Cr		ClOH	ArN, CaN			CaC	
⁵⁹ Cr	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn ⁺⁺
⁶³ Cu	TiO, PO ₂	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
⁶⁵ Cu	TiO	TiOH	VN	SiCl	SS, SO ₂ H	CrC	
²⁰⁸ Pb							
²⁰⁶ Pb							
²⁰⁷ Pb							
²⁰⁴ Pb							
⁵⁵ Mn	KO	ArOH	KN		NaS	CaC	Cd ⁺⁺

TABLE II: (cont.) Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
²⁰² Hg	WO						
²⁰⁰ Hg	WO	WOH	WN				
¹⁹⁹ Hg	WO	WOH					
²⁰¹ Hg		WOH					
¹⁹⁸ Hg	WO	TaOH	WN			WC	
²⁰⁴ Hg							
¹⁹⁶ Hg			WN				
⁵⁸ Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd ⁺⁺ , Sn ⁺⁺
⁶⁰ Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn ⁺⁺
⁶² Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn ⁺⁺
⁶¹ Ni	SeO	CaOH	TiN	MgCl	SiS	TiC	
⁶⁴ Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
⁸⁰ Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
⁷⁸ Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
⁸² Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
⁷⁶ Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
⁷⁷ Se	NiO	CuN	CuN	CaCl, ArCl	ScS	CuC	
⁷⁴ Se	NiO	NiN	NiN	ClCl, KCl	CaS	NiC	
¹⁰⁷ Ag	ZrO	ZrOH		GeCl	AsS	MoC	
¹⁰⁹ Ag		MoOH	MoN	GeCl	SeS	MoC	
²⁰⁵ Tl							
²⁰³ Tl		WOH					
⁵¹ V	ClO	SOH	CiN	ClO, CiN	FS	KC	
⁵⁰ V	SO		ArN			ArC	Mo
⁶⁴ Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
⁶⁶ Zn	TiO	TiOH	CrN	PCl, SiCl	SS	FeC	
⁶⁸ Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba ⁺⁺
⁶⁷ Zn	VO	TiOH, Cr	CrN	SCl	CiS	MnC	Ba ⁺⁺
⁷⁰ Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

Note: The information provided in this table does not indicate that all of the described interferences need to be tested. However, the table can be consulted for informational purposes if unusual samples are encountered.

Table III: Mass Choices

Element of Interest	200.8 Reported Mass	200.8 Masses for Monitoring Purposes Only	6020A Reported Mass	6020A Masses for Monitoring Purposes Only
Aluminum	<u>27</u>		<u>27</u>	
Antimony	<u>123</u>	121	<u>123</u>	121
Arsenic	<u>75</u>		<u>75</u>	
Barium	135	<u>137</u>	<u>135</u>	138, 137, 136, 134
Beryllium	<u>9</u>		<u>9</u>	
Boron	10	11	10	11
Cadmium	114	106, 108, <u>111</u>	<u>114</u>	112, <u>111</u> , 110, 113, 116, 106
Calcium	<u>44</u>	42, 43, 46, 48	<u>44</u>	42, 43, 46, 48
Chromium	<u>52</u>	53	<u>52</u>	<u>53</u> , <u>50</u> , 54
Cobalt	<u>59</u>		<u>59</u>	
Copper	<u>63</u>	65	<u>63</u>	<u>65</u>
Iron	<u>57</u>	<u>56</u>	<u>57</u>	<u>56</u> , <u>54</u> , <u>58</u>
Lead	<u>208</u>	<u>206</u> , <u>207</u>	<u>208</u>	<u>207</u> , <u>206</u> , 204
Magnesium	(26)	(24, 25)	<u>26</u>	24, <u>25</u>
Manganese	<u>55</u>		<u>55</u>	
Molybdenum	97	95, <u>98</u>	<u>97</u>	98, 96, 92, 94, 108
Nickel	<u>60</u>	62	<u>60</u>	58, 62, <u>61</u> , 64
Potassium	(39)		<u>39</u>	
Selenium	<u>82</u>	78 (not 77)	<u>82</u>	78
Silica	28		28	
Silver	<u>107</u>	109	<u>107</u>	<u>109</u>
Sodium	(23)		<u>23</u>	
Thallium	<u>205</u>	203	<u>205</u>	203
Titanium	47		47	
Uranium	<u>238</u>		(238)	
Vanadium	<u>51</u>		(51)	
Zinc	<u>66</u>	67, 68	<u>66</u>	64, <u>68</u> , <u>67</u> , 70
Tin	118		<u>118</u>	120
Chlorine*		(35, 37, 77, 82)		35, 37, 77, 82
Lanthanum*		(139)		139
Thorium*		<u>232</u>		(232)
Krypton*		83		(83)
Ruthenium*		99		(99)
Palladium*		105		(105)

Note: Elements other than those of interest are monitored to indicate other potential molecular interferences, which could affect the data quality. Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined (recommended for determination by 200.8 & 6020A) and in boldface (6020A).

*Elements that are mass calibrated only and are monitored for their possible interfering effects with the reported elements. The starred items are not reported.

Ion 78 is used for Selenium monitoring instead of the method suggested 77 (as is allowed per the method) due to instrument configuration (ion 77 is used for argon chloride correction). Ion 135 is used for Barium reporting (as suggested by 6020A, and allowed per 200.8) instead of the 200.8 method suggested 137.

Table IV: Tuning Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below are suggested solutions which cover a typical mass calibration range.

Element	Concentration (µg/L)
Be	10
Ce	10
Co	10
In	10
Mg (3 lines)	10
Pb (3 lines)	10

Table V: Suggested Tuning and Response Factor Criteria

Minimum Response from Tuning Solution With a Peristaltic Pump Speed of 35-40 RPM:

Be	>5,000
Mg	>10,000
Co	>50,000
In	>90,000
Pb	>10,000

Suggested Mass Calibration:

Be	9
Mg	24, 25, 26
Co	59
In	115
Pb	206, 207, 208

Table VI: Quality Control (QC) Requirements and SW-846 (SOP) / EPA Terminology Equivalents

Shealy QC Parameter	EPA Method 6020A / 200.8 Equivalent	Definition / Frequency	Acceptance Criteria	Corrective Action	Acronym Equivalents
Method Blank	6020A: Prep Blank	Assess contamination / Every batch of 20 samples or less	< RL or <5 % Reg limit or < 10x sample results (whichever is higher)	Re-digest and reanalyze samples. Refer to section 9.4 of SOP for additional requirements	MB = PB MB = LRB
	200.8: Laboratory Reagent Blank		200.8 SDW: <1/2 PQL or <10 % sample conc.		
Laboratory Control Sample	6020A: LCS	Standards added to a LRB (same prep as samples) / Every batch of 20 samples or less	6020A: ± 20 %	Re-digest and reanalyze samples	LCS = LFB (4 LCSs are used for the IDOC)
	200.8: Laboratory Fortified Blank		200.8: ± 15 %	Refer to section 9.5 of SOP	
Matrix Spike	6020A: MS	Known amount of analyte added to a duplicate sample / Every 10 % or each batch, whichever is less frequent	75-125 %	Refer to section 9.6 of SOP for additional requirements	MS = LFM
	200.8: Laboratory Fortified Matrix				
Initial Calibration Verification	6020A: ICV	Second source standard, verifies ICAL / after ICAL	± 10 %	Terminate analysis; correct the problem; recalibrate	ICV = QCS (4 QCSs are used for the IDOC)
	200.8: Quality Control Standard	Second source standard, verifies ICAL / initial set up, then quarterly			
Continuing Calibration Verification	6020A: CCV	after every ten samples, and end of sequence	6020A: ± 10 %	If unacceptable, correct the problem, recalibrate the instrument, re-verify calibration and rerun all samples associated with unacceptable CCV's	CCV = IPC
	200.8: Instrument Performance Check	200.8: Verifies ICAL / Immediately following the ICAL, every ten samples, and end of sequence	200.8: ± 10 %, if CCV is ± 15 %, report previous samples and recalibrate		

Table VI (cont.) QC Requirements and SW-846 (SOP) / EPA Terminology

Shealy QC Parameter	EPA Method 6020A / 200.8 Param'r	Definition / Frequency	Acceptance Criteria	Corrective Action	Acronym Equivalents
Initial Calibration Blank	6020A: ICB	Analyte free Reagent Water / Immediately after second source standard	<reporting limit	Terminate analysis; correct the problem; recalibrate	ICB
	200.8: None				
Continuing Calibration Blank	6020A: CCB	Analyte free Reagent Water / Immediately following each CCV/IPC	<reporting limit	Terminate analysis; correct the problem; recalibrate	CCB
	200.8: None				
Low Level Initial Calibration Verification	6020A: None	Standard containing all analytes at the RL concentration / Once per ICAL	±30 %	Recalibrate, or, do not report that element from this run	LLICV
	200.8: None				
Internal Standard	6020A: IS	Measures relative responses of other elements / Every analysis	6020A: 30-120 % of Calibration blank intensity	Dilute and re-analyze	IS
	200.8: IS		200.8: 60-125 % of Calibration blank intensity		
Interference Check Solution A	6020A: ICSA	Contains 8 Interfering Elements (Ref. App A for concentrations) / After ICAL (before samples) and every 12 hours	±50 % for Spiked Elements ±2xPQL or <1ppb for Non-Spiked	Refer to section 9.11 of SOP	ICSA
	200.8: None				
Interference Check Solution AB	6020A: ICSAB	Contains 8 Interfering Elements and 11 analytes / After ICAL (before samples) and every 12 hours	±50 % for Spiked Elements ±2xPQL or <1ppb for Non-Spiked	Refer to section 9.11 of SOP	ICSAB
	200.8: None				
Serial Dilution	6020A: Dilution Test	5x dilution / One sample per batch	±10 %	Flag Data	SD
	200.8: None				
Post-Digestion Spike	6020A: PDS	Spike added to a digested sample / If MS fails criteria	80-120 %	Flag Data	PDS
	200.8: None				

TABLE VII. Method 200.8 and 6020A ICP-MS Target Analyte List and PQLs

ELEMENT	Symbol	CAS #	RCRA 6020A Analyte	SDWA 200.8 Analyte	CWA 200.8 Analyte	PQL (ug/L) Aqueous
Aluminum	Al	7429-90-5	X	X	X	40
Antimony	Sb	7440-36-0	X	X	X	1.0
Arsenic	As	7440-38-2	X	X	X	1.0
Barium	Ba	7440-39-3	X	X	X	5.0
Beryllium	Be	7440-41-7	X	X	X	0.40
Boron	B	7440-42-8	X*	X*	X	25
Cadmium	Cd	7440-43-9	X	X	X	0.10
Calcium	Ca	7440-70-2	X*	X*	X*	200
Chromium	Cr	7440-47-3	X	X	X	5.0
Cobalt	Co	7440-48-4	X	X	X	5.0
Copper	Cu	7440-50-8	X	X	X	1.0
Iron	Fe	7439-89-6	X*	X*	X	20
Lead	Pb	7439-92-1	X	X	X	1.0
Magnesium	Mg	7439-95-4	X*	X*	X	50
Manganese	Mn	7439-96-5	X	X	X	5.0
Molybdenum	Mo	7439-98-7	X*	X	X	10
Nickel	Ni	7440-02-0	X	X	X	5.0
Potassium	K	7440-09-7	X*	X*	X	200
Selenium	Se	7782-49-2	X*	X	X	1.0
Silica by Si	SiO ₂	7440-21-3	X*	X*	X*	220
Silicon	Si	7440-21-3	X*	X*	X*	100
Silver	Ag	7440-22-4	X	X	X	1.0
Sodium	Na	7440-23-5	X*	X*	X	200
Thallium	Tl	7440-28-0	X	X	X	0.50
Tin	Sn	7440-31-5	X*	X*	X	5.0
Titanium	Ti	7440-32-6	X*	X*	X*	5.0
Uranium	U	7440-06-11	X*	X*	X*	50
Vanadium	V	7440-62-2	X*	X*	X	5.0
Zinc	Zn	7440-66-6	X	X	X	10

† Note that the CFR has not yet approved ICP-MS for CWA analysis. The EPA, Region IV, has granted Shealy approval to do so. The elements with * in this column, are not listed as analytes of interest by SCDHEC, and therefore, are not certifiable in the state of South Carolina.

*Not an element that is listed in the Code of Federal Regulations (CFR) by ICP-MS per that program area (not certifiable by DHEC).

TABLE VIII. MS/MD and LCS/D Spike Levels

ELEMENT	(ug/L)
Aluminum	100
Antimony	100
Arsenic	100
Barium	100
Beryllium	100
Boron	100
Cadmium	100
Calcium	1000
Chromium	100
Cobalt	100
Copper	100
Iron	1000
Lead	100
Magnesium	1000
Manganese	100
Molybdenum	100
Nickel	100
Potassium	1000
Selenium	100
Silica by Si	220
Silicon	1000
Silver	100
Sodium	1000
Thallium	100
Tin	100
Titanium	100
Uranium	100
Vanadium	100
Zinc	100

TABLE IX. ICP-MS Calibration Standards

ELEMENT	Cal. Level 1 (ug/L)	Cal. Level 2 (ug/L)	Cal. Level 3 (ug/L)	Cal. Level 4 (ug/L)	Cal. Level 5 (ug/L)	Cal. Level 6 (ug/L)
Aluminum	40	200	250	500		
Antimony	1.0	5.0	250	500		
Arsenic	1.0	5.0	250	500		
Barium	5.0	25	250	500		
Beryllium	0.4	2.0	250	500		
Boron	25	125	250	500		
Cadmium	0.1	0.5	250	500		
Calcium	200		250	500	50000	100000
Chromium	1.0	5.0	250	500		
Cobalt	5.0	25	250	500		
Copper	1.0	5.0	250	500		
Iron	20	100	250	500	50000	100000
Lead	1.0	5.0	250	500		
Magnesium	50		250	500	50000	100000
Manganese	5.0	25	250	500		
Molybdenum	10	50	250	500		
Nickel	5.0	25	250	500		
Potassium	200		250	500	50000	100000
Selenium	1.0	5.0	250	500		
Silicon	100		250	500	5000	10000
Silver	1.0	5.0	250	500		
Sodium	200		250	500	50000	100000
Thallium	0.5	2.5	250	500		
Tin	5.0	25	250	500		
Titanium	5.0	25	250	500		
Uranium	50		250	500		
Vanadium	5.0	25	250	500		
Zinc	10	50	250	500		

TABLE X. ICP-MS Calibration Verification Standards

ELEMENT	ICV (ug/L)	CCV (ug/L)
Aluminum	200	300
Antimony	200	300
Arsenic	200	300
Barium	200	300
Beryllium	200	300
Boron	200	300
Cadmium	200	300
Calcium	40000	60000
Chromium	200	300
Cobalt	200	300
Copper	200	300
Iron	40000	60000
Lead	200	300
Magnesium	40000	60000
Manganese	200	300
Molybdenum	200	300
Nickel	200	300
Potassium	40000	60000
Selenium	200	300
Silicon	2000	3000
Silver	200	300
Sodium	40000	60000
Thallium	200	300
Tin	200	300
Titanium	200	300
Uranium	200	300
Vanadium	200	300
Zinc	200	300

TABLE XI. Interference Check Sample Concentrations

ELEMENT	ICSA (ug/L)	ICSAB (ug/L)
Aluminum	100000	5000
Antimony		100
Arsenic		100
Barium		100
Beryllium		100
Boron		100
Cadmium		100
Calcium	100000	100000
Chromium		100
Cobalt		100
Copper		100
Iron	100000	100000
Lead		100
Magnesium	100000	100000
Manganese		100
Molybdenum	2000	2000
Nickel		100
Potassium	100000	100000
Selenium		100
Selenium		100
Silicon		
Silver		100
Sodium	100000	100000
Thallium		100
Tin		100
Titanium	2000	2000
Uranium		100
Vanadium		100
Zinc		100

APPENDIX B METALS DATA REVIEW CHECKLIST

ICP-MS Data Review Checklist

Preparation Batch #(s): _____

Instrument ID #: _____

Analytical Batch #: _____

Date: _____

Area of Review	Level I Review (Y/N)	Level II Review (Y/N)
• Prepared and analyzed per Method / SOP		
• Performance Check		
• Initial calibration correct		
• Internal Standard within criteria (6020A=30-120 %; 200.8=60-125 %)		
• QCS/IPC (=ICV/CCV) criteria met (± 10 %)		
• ICB/CCB criteria met (<RL)		
• ICSA/ICSAB met criteria		
• Analysis within linear range		
• LCS criteria met (6020A=80 %-120 %; 200.8=85 %-115 %)		
• MB criteria met PQL or sample is 10x blank result)		
• MS and/or MS/MD Recovery criteria met (75 % - 125 %)		
• MS/MD RPD criteria met (20 %)		
• % RSD criteria met for samples		
• % RSD criteria met for QC		
• Upload sheets reviewed for correct dilutions, results, etc.		
Initials		
Date		

MIO: Monitoring Ion Only, this ion is not used for reporting purposes

ENR: Element Not Requested, client does not need this element

DNR: Do Not Report, ion has failed criteria, it is not reportable

Comments: _____

APPENDIX C

TROUBLESHOOTING GUIDE

PROBLEM	POSSIBLE CAUSE/ SOLUTION
High Blanks	<p>Increase rinse time.</p> <p>Clean or replace tip.</p> <p>Clean or replace torch.</p> <p>Clean or replace sample tubing.</p> <p>Clean or replace nebulizer.</p> <p>Clean or replace mixing chamber.</p> <p>Lower torch.</p>
Instrument Drift	<p>RF not cooling properly.</p> <p>Vacuum level is too low.</p> <p>Replace torch (crack).</p> <p>Clean or replace nebulizer (blockage).</p> <p>Check room temperature (changing).</p> <p>Replace pump tubing.</p> <p>Room humidity is too high.</p> <p>Clean torch tip (salt buildup).</p> <p>Check for argon leaks.</p> <p>Adjust sample carrier gas.</p>
Erratic Readings, Flickering Torch or High RSD	<p>Check for argon leaks.</p> <p>Adjust sample carrier gas.</p> <p>Replace tubing (clogged).</p> <p>Check drainage (back pressure changing).</p> <p>Increase uptake time (too short).</p> <p>Increase flush time (too short).</p> <p>Clean nebulizer, torch or spray chamber.</p> <p>Increase sample volume introduced.</p> <p>Check that autosampler tubes are full.</p> <p>Sample or dilution of sample not mixed.</p> <p>Realign torch.</p> <p>Reduce amount of tubing connectors.</p>
Standards reading twice normal absorbance or concentration.	<p>Incorrect standard used.</p> <p>Incorrect dilution performed.</p>

APPENDIX D

CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered gloves must not be used in the metals laboratory since the powder contains silica and zinc as well as other metallic analytes. Only Non-powered, vinyl, or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

APPENDIX DoD-- QSM Requirements

Sections found in this appendix replace existing sections and apply solely to analyses for the Department of Defense-NFSEC. Some sections in this appendix may contain information to be added to existing main sections addressing any additional requirements of NFSEC.

9.0 QUALITY CONTROL

9.4 Method Blank Acceptance Criteria – replaces Section 9.4 and 9.4 sub-sections.

9.4.1 Method Blank (MB) – One method blank must be processed with each preparation and/or analytical batch. The method blank consists of a similar matrix to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results. The method blank is to contain all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

9.4.1 For a method blank to be acceptable for use with the accompanying samples, the concentration of analytes detected in the blank should be \leq one-half (1/2) the practical quantitation limit (PQL) or project specific reporting limits.

9.4.1.1 The acceptance criterion for common laboratory contaminants is that no analytes should exceed the PQL.

9.4.2 If the MB does not meet the criteria above, the source of the contamination shall be investigated and measures taken to minimize or eliminate the problem and affected samples reprocessed or data shall be appropriately qualified. All steps taken to return the system to control must be fully documented.

9.4.2.1 If reanalysis is not possible due to limited sample volume or holding time, then the samples associated with the contaminated blank must be evaluated as to the best corrective action for the samples (e.g., reprocessing or data qualifying codes). In all cases, the corrective action(s) must result in the completion of an NCM.

9.4.5 For DoD samples, no analyte must be detected at concentrations greater than 2 X the MDL in the CCB which is analyzed before beginning a sample run, after every 10 samples, and at the end of the analysis sequence

9.12 Analysis Carryover Study – The analysis carryover study must be performed on an annual basis per technology per instrument model. The study will also need to be repeated after any changes have been made (e.g. instrument conditions) that could affect the carryover. The carryover study demonstrates the concentration at which a target or non-target analyte may be detected without contaminating the subsequent sample (s). A carryover verification standard (CVS) is analyzed at the same concentration as the linear dynamic range (LDR) standard and will be followed immediately by an instrument blank. The maximum carryover criteria are as follows:

9.15.1 The resultant carryover must be $\leq \frac{1}{2}$ the applicable PQL.

9.15.2 If a sample is nondetect after being analyzed immediately after a sample with high concentrations of target and/or non-target compound(s), the sample results may be reported.

Additional studies may be performed to identify how many blanks are required in the contiguous sequence to achieve the $\leq \frac{1}{2}$ PQL criteria. These studies need to be fully documented and readily available to all analysts.

9.6 and 13.6 For DoD samples, the matrix spike and matrix spike duplicate control limits are 80-120 %.

9.10.2 For DoD analysis, when the ICS-A is run, the absolute value of concentration for all non-spiked analytes must be $< 2 \times \text{MDL}$, unless higher values found are verified trace impurity from one of the spiked analytes. The ICS-AB values must be within 80-120 % of the expected value.

9.2.2 For DoD work, the detection limits established from the IDL study must be $\leq \text{MDL}$.

10.5.1 Lower Order of Quantitation (LOQ) Verification – This is an analysis of a QC sample containing the analytes of interest in each matrix 1-2 times the claimed LOQ

10.5.1.1 A successful analysis is one where the recovery of each analyte is within the established test method acceptance criteria or client data quality objectives for accuracy.

10.5.1.2 This single analysis is not required if the bias and precision of the measurement system is evaluated at the LOQ.

10.5.1.3 The LOQ must not be set any lower than the low-level calibration standard for multi-point calibration or no lower than a low-level calibration check sample for single level calibration.

TABLE I. DoD Method 6020A ICP-MS Target Analyte List and PQLs

ELEMENT	Symbol	CAS #	PQL (ug/L) Aqueous
Aluminum	Al	7429-90-5	40
Antimony	Sb	7440-36-0	1.0
Arsenic	As	7440-38-2	1.0
Barium	Ba	7440-39-3	5.0
Beryllium	Be	7440-41-7	0.40
Cadmium	Cd	7440-43-9	0.10
Calcium	Ca	7440-70-2	200
Chromium	Cr	7440-47-3	5.0
Cobalt	Co	7440-48-4	5.0
Copper	Cu	7440-50-8	1.0
Iron	Fe	7439-89-6	20
Lead	Pb	7439-92-1	1.0
Magnesium	Mg	7439-95-4	50
Manganese	Mn	7439-96-5	5.0
Molybdenum	Mo	7439-98-7	10
Nickel	Ni	7440-02-0	5.0
Potassium	K	7440-09-7	200
Selenium	Se	7782-49-2	1.0
Silver	Ag	7440-22-4	1.0
Sodium	Na	7440-23-5	200
Thallium	Tl	7440-28-0	0.50
Vanadium	V	7440-62-2	5.0
Zinc	Zn	7440-66-6	10

Appendix N
Laboratory SOPs

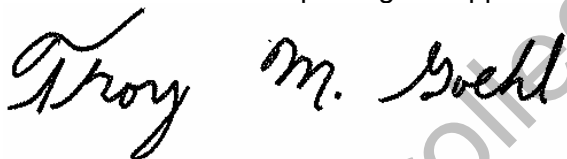
Microbac SOP
Hg-1631, Revision 2

Total and Dissolved Mercury
By EPA 1631

STANDARD OPERATING PROCEDURE FOR MERCURY USING AUTOMATIC FLUORESCENCE SPECTROSCOPY

Revision Author: Randon Lingenfelter

This SOP is effective upon signed approval by the following:



8/7/2009

Inorganics Manager

Date



QA/QC Manager

8/28/2009

Date

DISCLAIMER: This SOP has been developed for use at the Microbac Laboratories, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

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2.0 SCOPE AND APPLICATION

- 2.1 This is an atomic fluorescence spectroscopy procedure for the determination of Mercury. This procedure is applicable and restricted to the analysis of aqueous matrix samples. The applicable analytes, detection limits and routine reporting limits (PQL) are listed at the Limits tab of the applicable test codes in LIMS.

3.0 SUMMARY

- 3.1 The integrity of this procedure is maintained only through the application of proper sample collection, sample handling, storage and analysis using the “clean hands, dirty hands” technique.
- 3.2 In the container received, the entire sample is oxidized with Bromine monochloride (BrCl) at a ratio of 5-ml BrCl per 500-ml sample. The sample is allowed to oxidize all available Hg to Hg(II) for a minimum of 24-hours. 50-ml of oxidized sample is analyzed where it is sequentially reduced with Hydroxylamine monochloride (NH₂OH · HCl) to destroy the free halogens, then with stannous chloride (SnCl₂) to convert Hg(II) to volatile Hg(0). The Hg(0) is separated from solution by purging and vapor/liquid separation.
- 3.3 This procedure is based on the reference methods listed in section 17 of this document. This procedure contains no significant deviations to the reference method.

4.0 DEFINITIONS

- 4.1 A list of definitions is in the Quality Assurance Plan.

5.0 INTERFERENCES

- 5.1 Preventing samples from becoming contaminated during the sampling and analysis process constitutes one of the greatest difficulties encountered in trace metals determinations. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing samples for trace metals.
- 5.2 Samples may become contaminated by numerous routes. Potential sources of contamination include sampling protocol, containers, sampling equipment, labware, reagents, and atmospheric inputs such as dirt and dust. Even human contact can be a source of contamination.

5.3 Contamination Control

- 5.3.1 Philosophy – The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is free from any material that may contain mercury. Substances in a sample cannot be allowed to contaminate the laboratory work area or instrumentation used for trace Mercury measurements.

- 5.3.2 Avoiding contamination – The best way to control contamination is to completely avoid exposure of the sample to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being done.
- 5.3.3 Use a clean environment – The Mercury clean room has been designed to minimize (if not ultimately eliminate) Mercury contamination from outside sources. Incoming air is appropriately filtered and the airflow designed to pass clean air from the instrument lab into and through the preparation lab. Access is restricted to authorized and trained personnel only. Appropriate sample receipt protocols are used to ensure that only non-externally contaminated samples are brought into the lab. Sample receipt into the lab is by way of an isolated holding area to allow for proper cleaning of sample containers prior to handling inside the preparation lab.
- 5.3.4 Wear gloves – Analysts must wear clean, non-talc gloves during all operations involving handling of the samples, reagents and standards.
- 5.3.5 Contamination by carryover – Contamination may occur when a sample is processed immediately after a sample containing a relatively high concentration of Mercury. The Hg concentration at which the analytical system (purge, traps, and detector) will carry greater than 0.5 ng/L of Hg into a succeeding system blank must be determined (see the QA/QC section).

5.4 Interference

- 5.4.1 At the time of promulgation of the reference method, gold and iodide were known interferences. At a Mercury concentration of 2.5 ng/L and at increasing iodide concentrations ranging from 30 to 100 mg/L, test data have shown that Mercury recovery will be reduced from 100 to 0 percent. At iodide concentrations greater than 3 mg/L, the sample should be pre-reduced with SnCl_2 (to remove the brown color) and additional or more concentrated SnCl_2 should be added. To preclude loss of Hg, the additional SnCl_2 should be added in a closed vessel or analysis should proceed immediately. If samples containing iodide concentrations greater than 30 mg/L are analyzed, it may be necessary to clean the analytical system with 4N HCl after the analysis.

6.0 SAFETY

- 6.1 Consult the current revision of the Chemical Hygiene Plan. Requirements for the use of personal protective equipment (e.g. safety glasses, lab coats, gloves) as well as other area-specific safety requirements (e.g. gas cylinders) and MSDS sheets are addressed in the CHP.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

- 7.1 All volumetric glassware used shall be ASTM Class A. Class B glassware must be verified for accuracy on an annual basis and labeled with an appropriate correction.
- 7.2 All reagent and standard preparation must be performed in the mercury-free clean room.
- 7.3 PPE: latex gloves (Fisher #11-394-5C or equivalent); lab coat and safety glasses as specified in the Chemical Hygiene Plan
- 7.4 Tackymat: Fisher #06-520-5
- 7.5 Glassware: 100-ml and 1000-ml volumetric flasks
- 7.6 Pipettes: 10 – 100- μ l and 100 – 1000- μ l adjustable volume repipettors
- 7.7 Digestion/Autosampler tubes: SCP Science product, Fisher #S195-500 or equivalent
- 7.8 Instrument: CETAC M8000
- 7.9 SCP Digifilter Manifold #010-500-230
- 7.10 SCP 0.45-micron Digifilters #010-500-070

8.0 REAGENTS AND STANDARDS

- 8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST, when available. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

All reagents are stored in the mercury-free clean room unless otherwise noted. Unless otherwise noted, prepared reagents are stored in appropriate containers, retained in the clean room and prepared on an as needed basis.

- 8.2.1 Lab pure water (DI water): Analyte free water is prepared as described in the Quality Assurance Plan. DI water is obtained from the designated tap in the clean-room.
- 8.2.2 Hydrochloric acid, concentrated: Fisher catalog #A508-212 or equivalent.
- 8.2.3 Nitric acid, concentrated: Fisher catalog #A509-212 or equivalent

- 8.2.4 Instrument rinse, 1%: In a 2L fluoropolymer bottle (supplier by CETAC) dilute 20-ml Bromine Monochloride solution to a final volume of 2L with lab pure water. Prepare this reagent on a daily basis.
- 8.2.5 Bromine Monochloride: In a clear glass jar, combine 1 packet of BrCl solution (Environmental Express #HP9010 or equivalent) and 90-ml concentrated HCl. Prepare fresh monthly.
- 8.2.6 Hydroxylamine Hydrochloride: In a 250-ml container, dissolve and dilute 75-g Hydroxylamine Hydrochloride (Fisher #H330-1 or equivalent) to the mark with lab pure water. Prepare fresh monthly.
- 8.2.7 Stannous Chloride: In a 1L container, dissolve and dilute 200g of Stannous Chloride crystals (Fisher #T142-500 or equivalent.) with 100-ml concentrated HCl and lab pure water. Prepare fresh weekly.
- 8.2.8 10% HCl rinse solution: In a Digitube, dilute 5-ml of conc. HCl to 50-ml with DI water.
- 8.2.9 10% HNO_3 rinse solution: In a Digitube, dilute 5-ml of conc. HNO_3 to 50-ml with DI water.

8.3 Standards

All standards are stored in the mercury-free clean room unless otherwise noted.

- 8.3.1 Stock Calibration standard, 1000 mg/l: SPEX catalog # PLHG4-2Y or equivalent.
- 8.3.2 Intermediate Calibration standard, 1 mg/l: In a 100-ml volumetric flask, dilute 0.1-ml of the stock calibration and 7-ml of 7% HCl to the mark with lab pure water. Prepare fresh monthly.
- 8.3.3 Working Calibration standard A, 1 ug/l: In a 100-ml volumetric flask, dilute 0.1-ml of the intermediate calibration standard and 7-ml of 7% HCl to the mark with lab pure water. Prepare fresh monthly.
- 8.3.4 Calibration curve: Prepare the following dilutions in individual 50-ml digestion tubes using 0.50-ml BrCl and lab pure water. The calibration curve standards should be prepared fresh with each calibration. The calibration (system) blanks are prepared by filling a 500-ml sample container with lab pure water, acidifying with 2.5-ml conc. HCl and oxidizing with 5.0-ml BrCl.

Vol. (ml)	Parent Std	Final Conc., ng/l
5.0	Working Cal Std A	100
2.5	Working Cal Std A	50
1.25	Working Cal Std A	25
0.25	Working Cal Std A	5.0
.025	Working Cal Std A	0.5
0 ---		0

- 8.3.5 Method Blank: In a 500-ml clean bottle add the same reagents as the prep batch and fill with DI water.
- 8.3.6 IPR / OPR: This is the same as the 5.0-ng/l standard used for instrument calibration.
- 8.3.7 MS/MSD, 5-ng/l: Add 0.25-ml of the working calibration standard A to 50-ml sample.
- 8.3.8 Stock Verification standard, 1000 mg/l: CPI catalog # S4400-1000331 or equivalent. This standard must be of a source different than that used for calibration.
- 8.3.9 QCS Intermediate standard, 1 mg/l: In a 100-ml volumetric flask, dilute 0.1-ml of the stock verification standard and 7-ml of 7% HCl to the mark with lab pure water. Prepare fresh monthly.
- 8.3.10 QCS Working Standard A, 1-ug/l: In a 50-ml volumetric flask, dilute 0.05-ml of the QCS intermediate standard and 3.5-ml of 7% HCl to the mark with lab pure water. Prepare fresh monthly.
- 8.3.11 QCS, 5.0 ng/l: In a 50-ml digestion tube, dilute 0.25-ml of the QCS working standard A to 50-ml with 0.5-ml BrCl and lab pure water. Prepare fresh with each calibration.

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

- 9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted. Samples must be received inside of a double-bag system. The outer bag is considered a dirty bag and the inner bag a clean bag. Refer to the Sample Receipt and Login SOP for details. Samples not received in this manner will be rejected or the discrepancies noted and reported to the client.
- 9.2 Samples should be collected in a glass container. No thermal or chemical preservation is required during transit. Refer to the Sample Receipt and Login SOP for the criteria used at sample receipt to determine whether or not the sample integrity has been maintained. Samples are stored in the double-door staging area built into the mercury-free clean room. Samples that fail to meet the receipt criteria will be rejected or noted as such on the Cooler Inspection Report during the Login process.
- 9.3 Chemical preservation is applied as part of the preparation procedure. See the details in the Procedure section.
- 9.4 Provided that samples are received unpreserved then acidified and oxidized full volume (as described in the procedure section), the maximum allowable hold times are: acidification within 28-days and analysis within 90-days of collection.

10.0 QUALITY CONTROL

- 10.1 An *Initial Precision & Recovery (IPR)* study must be performed prior to the initial implementation within the lab and whenever substantial change has occurred in the procedure or instrument. Analyze four consecutive 5 ng/l calibration standards. Submit the data to the QA department for evaluation. Refer to EPA Method 1631E section 9.2.2 for details.
- 10.2 A *Method Detection Limit (MDL)* study must be performed for each new analyst, annually thereafter, and whenever a significant change in procedure or instrument occurs. Analyze a minimum of seven (maximum of ten) standards prepared in the range of 0.1-1.0 ng/l. These standards must be taken through the entire analytical procedure. Submit the data to the QA department for evaluation. Refer to EPA Method 1631E section 9.2.1 for details.
- 10.3 A *Carryover Point* study must be performed prior to the initial implementation within the lab and whenever substantial change has occurred in the instrument. The carryover point is the Hg concentration at which the analytical system will carry greater than 0.5 ng/L of Hg into a succeeding system blank. This concentration may be determined by analyzing calibration solutions containing successively larger concentrations of Hg. When an environmental sample contains $\frac{1}{2}$ or greater of this determined Hg concentration, a system blank must be analyzed to demonstrate no carryover at the blank criteria level. Preferably, if analysis of the high calibration standard does not result in the carryover of more than 0.5 ng/l into a succeeding blank, the carryover point is defined as some concentration above the linear range of the instrument and any environmental sample having a Mercury concentration greater than that level must be diluted and reanalyzed. Samples that are known or suspected to contain a high concentration of Mercury should initially be analyzed at an appropriate dilution or after samples containing low or non-detectable levels.
- 10.4 An *On-going Precision and Recovery (OPR) Standard* must be analyzed immediately after calibration, after every 12 consecutive hours of analysis, and after the sample. The concentration of the OPR is defined in the reference method as 5 ng/L.
- 10.4.1 Acceptance criteria are defined in the reference method and listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.
- 10.4.2 OPR standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.
- 10.4.3 The reporting of data associated with a failed OPR must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.

- 10.4.4 Samples associated with an OPR that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.
- 10.5 A *Quality Control Sample (QCS)* must be analyzed prior to the analysis of environmental samples at a frequency of 1 per run. The QCS is prepared from a standard source different than that used for the OPR.
- 10.5.1 Acceptance criteria are nominally set to be the same as the OPR and are listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.
- 10.5.2 QCS' that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.
- 10.5.3 The reporting of data associated with a failed QCS must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.
- 10.5.4 Samples associated with an QCS that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.
- 10.6 A minimum of three *Method Blanks* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day.
- 10.6.1 The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.
- 10.6.2 MBLKs that fail to meet the acceptance criteria cause the sample results to be automatically flagged in LIMS with a "B" qualifier. MBLKs that are below the reporting limit but above the MDL are flagged in LIMS with a "b" qualifier. "b" flagged data is considered as meeting the acceptance criteria.
- 10.6.3 The reporting of data associated with a failed control sample must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.
- 10.6.4 Samples associated with a MBLK that fails with positive bias can be reported without narration if the sample concentration is < PQL or greater than 10 times the blank contamination.
- 10.7 A *Matrix Spike and Matrix Spike Duplicate* sample must be prepared and analyzed with each batch of maximum 10 samples per matrix and at a minimum of one per day.

- 10.7.1 Acceptance criteria are defined in the reference method and listed in the appropriate test code in LIMS. (Note: the accuracy criteria have been met provided at least either the MS or MSD meet the %R criteria.) If the acceptance criteria are not met, refer to the MS/MSD Corrective Action Flowchart in the QAP.
- 10.7.2 MS/MSD's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier. MSD's that fail to meet the precision criteria are automatically flagged in LIMS with a "R" qualifier.
- 10.7.3 The reporting of data associated with a failed MS/MSD must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.
- 10.7.4 Samples associated with a MS/MSD that fails the accuracy criteria with positive bias can be reported without narration if the sample concentration is below the reporting limit.
- 10.7.5 If the concentration measured in the sample is greater than 4-times the concentration of the spike, the spike amount used is insufficient and the MS/MSD not applicable.

11.0 CALIBRATION AND STANDARDIZATION

Calibration data is documented and retained using the printouts from the instrument software and the report generated using the "1631 Calibration and QC Evaluation" spreadsheet. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

- 11.1 Instrument calibration is required each day of analysis for each run.
- 11.2 Perform the required preventative maintenance as necessary. Refer to the maintenance log book for M8000.
- 11.3 Open the QuickTrace file. A box will appear asking if you want the detector block temperature to stabilize. Choose Yes. This can take anywhere from 20 minutes to several hours depending on how long the instrument was off. The remainder of the program will open when the detector temperature has stabilized.
- 11.4 Create a new data file for the day. This is done by choosing *File, New From*. A box will open. Click the *Browse* button next to the template worksheet box. A file directory will open up. Choose *QuickTrace* file and then open the *Worksheets* file. Choose the template you wish to use (typically, use that from the previous day). When the worksheet is open, enter the name for the new worksheet using the naming convention "1631" followed by the date (e.g. 1631 11-10-03).
- 11.5 Check the tubing on the peristaltic pump for wear and replace if needed. Place the tubing on the pump in the following order from bottom to top: drain (large white-white tubing), autosampler (yellow-yellow tubing), stannous (black-black tubing), and finally the hydroxylamine tubing (red-blue) should be on the top. Turn the

pump on with the black switch on the front of the pump. Starting with the bottom clamp, apply tension with the locking arm. Check for good flow through the tube and proceed to the next clamp. Continue until all the clamps are locked into place and then recheck all of the flows.

- 11.6 Place the stannous and the hydroxylamine lines into the container of DI water next to the instrument.
- 11.7 The Gas Liquid Separator (GLS) must be wet to insure proper liquid gas separation. To do this, open the *instrument control panel* (this button has a screwdriver, hammer, and wrench on it). In the new window that opens up, click on the icon with 3 test tubes on it. This screen will have a gas control box on it. Set the gas flow to 40 and click set gas. Look inside the window at the GLS and make sure there are bubbles rising up. Pinch the drain line that goes into the peristaltic pump. This will cause the GLS to fill with water. Make sure that bubbles reach the top of the GLS to completely wet the center tube of the GLS. Repeat if proper wetting does not occur. An error message will appear on the computer screen and the peristaltic pump will stop. The error will say that a GLS overflow has occurred and to click yes to recover from it. Unpinch the drain tubing and click yes. This will allow all of the liquid to drain from the GLS. If the error shows up again repeat the steps listed to continue the draining of the GLS.
- 11.8 Remove the stannous and hydroxylamine lines from the DI water and place them into the appropriate containers. Let the instrument set for the couple minutes to stabilize with this new gas setting and close the instrument control box.
- 11.9 At this time the instrument needs to be profiled to make sure things are flowing and working properly. Open the *method editor* (icon looks like a book with a pencil on it). A new window will open. Click the button that has a green arrow pointing to a blue test tube. This will cause the instrument to zero. If necessary, the instrument will temperature stabilize as well. A new window will open up which shows a diagram of the autosampler. Place the 100 ng/L standard in a location and choose that location on the screen. The autosampler will move to that location and sample this standard. The graph on the computer screen will show the results of this standard. It will take approximately 6-minutes for the sample analysis to complete. When it is done look at the graph to make sure the instrument is reading the sample at the correct time. If this looks okay, look at the profile replicate RSD %. This percentage should be at less than 0.4. If this fails, repeat the peak profile. If it passes close, the method editor box.
- 11.10 To begin a calibration, open the *sequence editor* box (icon looks like a magic wand). On the sequence page, make sure the sample count is 0 and that the box next to "Begin with Calibration" is checked. Click on the *Auto QC* page and make sure all QC solutions are removed from the "QC Calibration Error Box". This will let the instrument calibrate and then stop. Click the *Generate Sequence* box. Another box will appear asking if you want to save the changes you have made, click Yes.
 - 11.10.1 The analyst has the option of entering the sample IDs. If performed, enter "0" for the number of samples in the run. Turn off OPR at the start and the end of the run.

- 11.11 Make sure all of the calibration standards are loaded into the autosampler. Hit the green "GO" button to start the calibration. Calibration will take approximately 1-hour to complete. After the calibration is done, the peristaltic pump will go to standby and a box telling you this has occurred will appear on the screen. Click Yes to remove the box, and look at the results of the calibration. If the calibration passed, the computer will give you a calibration factor as well as a calibration %RSD. If it fails, you will get a failure message and the calibration must be repeated. Analysis of environmental samples cannot proceed without the generation of an acceptable calibration.

- 11.11.1 The calibration acceptance criteria are as follows. The instrument software as well as the “1631 Calibration and QC Evaluation” spreadsheet is programmed to calculate and evaluate the calibration criteria.

- 3 system blanks
average
standard
 - Linearity CF
- <0.5 ng/l each
<0.5 ng/l
deviation <0.1 ng/l
 $m \leq 15\%$ RSD
75-125 %R for the PQL level standard

12.0 PROCEDURE

12.1 SAMPLE PREPARATION

Preparation data is documented and retained using the Mercury Prep Logsheet for EPA 1631E. Preparation data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

- 12.1.1 Samples are received through a double-door staging area built into the mercury-free clean room. Put on a new pair of clean gloves and bring the samples from the staging area into the prep lab. Process samples into the lab one at a time.

- 12.1.2 Open the bag, remove the sample container and rinse the container with lab pure water from the faucet. Place the bag in the trash and the rinsed bottle on a paper towel underneath the hood. Verify the sample label information and the physical condition of the sample container. Notify the Supervisor or Project Manager of any label inaccuracies. Note any container inadequacies such as cracked lids, bottles, etc.

- 12.1.3 Open the sample container and add conc. HCl at a ratio of 5-ml per 1L sample (2.5-ml per 500-ml sample container). If the container is completely filled with sample volume, be certain to thoroughly shake the sample and pour off a small volume prior to adding the acid. Cap the sample and mix.

- 12.1.4 Open the acidified sample container and add BrCl reagent at a ratio of 5-ml per 500-ml sample. Cap the sample and mix. NOTE: Be certain to evaluate the batch size as samples are processed. All samples from a given run must be processed with the same reagents.

- 12.1.5 Allow the samples to oxidize for a minimum of 24-hours prior to analysis.

12.2 SAMPLE ANALYSIS

Analytical data is documented and retained using the printouts from the instrument generated analytical report, run log, and the "1631 Calibration and QC Evaluation" spreadsheet. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

- 12.2.1 After the calibration has passed, create an autosampler table if it was not already created. To do this, click on the *sequence editor* box. On the sequence page, enter the number of samples that you will be analyzing and uncheck the "Begin with Calibration" box. On the "Auto QC" page, insert OPR standards at the beginning and end of analysis. Click the *generate sequence* button to make the table. The table will appear in a new window. In this window, type the sample ID for each sample that will be run from the sample prep log. After this is done, click the green "GO" button to start the run. If the OPR fails the run will stop; otherwise, the samples will run until completion. Make sure that there is plenty of rinse in the rinse bottle. Running out of rinse will cause the instrument to read erroneously low results and cause the QC samples to fail the applicable criteria.
- 12.2.2 When the run ends, print the run and the run log. Create a PDF file of the instrument run.
- 12.2.3 Remove the stannous and hydroxylamine lines and place them into the stannous line in 10% HNO₃ and the hydroxyl line in 10% HCl. Let this solution run through the instrument for 5-minutes to remove any salt buildup that may have occurred.
- 12.2.4 Place the lines into the bottle of DI water for 5-minutes to rinse the acid solution from the instrument.
- 12.2.5 Pull the lines from the DI rinse and place them in the empty bottle to let the liquid get removed from the lines.
- 12.2.6 Pull the rinse line from the bottle and place it in an empty 5000-ml bottle. Pump until all lines are dry.
- 12.2.7 Open the instrument controls and move the autosampler probe to the up position so that it is also pulling air through the lines.
- 12.2.8 Once all of the liquid has flushed out of the lines, put the instrument into standby by hitting the *standby button* (looks like a ¼ moon), and release the pump tubing to avoid excess stretching or manually turn off the pump and lamp.

13.0 CALCULATIONS AND DATA HANDLING

- 13.1 The instrument software, using the following equation, calculates the sample concentration.

$$\text{Conc., ng/L} = [(uabs_{\text{samp}} - \text{avg } uabs_{\text{blk}}) / CF_m] [(PFac) (DF)]$$

Where:

CF	$CF_m = \text{mean CF from all calibration standards}$
PFac	$= (uabs_{\text{std}} - \text{avg } uabs_{\text{blk}}) / \text{conc}_{\text{std, ng/l}}$
DF	$= \text{preparation factor} = V_f / V_i$
	$= \text{dilution factor}$

- 13.2 LIMS calculates the final sample concentration as follows:

$$\text{Mercury, ng/L} = (C) (DF) (Pfac)$$

Where: C = concentration from curve
DF = dilution factor (prior to adding sample to vial)
Pfac = (Final Volume, ml) / (Sample Size, ml)

- 13.3 After review, enter final results into the LIMS system. Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. There is less certainty in these data and, if sufficient sample and holding time are available, should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data are in the Analytical Data Entry – Metals SOP.

14.0 METHOD PERFORMANCE

- 14.1 Initial Demonstration of Capability study data, Method Detection Limit study data and Performance Testing study data are maintained and available from the QA office.

15.0 POLLUTION PREVENTION

- 15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.
- 15.2 Prepare the minimum amount of reagent and standard necessary.

16.0 WASTE MANAGEMENT

- 16.1 Refer to the Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

17.0 REFERENCES

17.1 USEPA Method 1631E

17.2 CETAC QuickTrace Mercury Analyzer software manual, part #480114, version 1.0

17.3 Microbac Laboratories Quality Assurance Plan, current revision, all sections

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

Copy of the Mercury Prep Logsheet for EPA 1631E (1 page)

Copy of the 1631 Calibration and QC Evaluation report (1 page)

Copy of the M8000 Maintenance Log (1 page)

SOP Revision Notification Form denoting changes made to this revision. (1 page)

Appendix to Method 1631 Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation

Uncontrolled Copy

Microbac Laboratories - Chicagoland Division
MERCURY PREP LOG SHEET - EPA 1631E

Analyst: _____ Batch ID: _____

	STD / Reagent ID	Exp. Date	Conc.
HCl	_____	_____	---
BrCl	_____	_____	---
Spike Standard	_____	_____	_____

Date/Time Samples Available: _____

	Sample ID	Cont ID	Date/Time HCl & BrCl Added	MS**	MSD**	Comments
MBLK 1						
MBLK 2						
MBLK 3						
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						

revision: b_12-03

* - HCl and BrCl added at a ratio of 5 mL each per 1L sample (1.25 mL/250 mL)

** - MS/MSD prepared in 50 mL volumes

Microbac Laboratories, Inc. – Chicagoland Division

1631 Calibration and QC Evaluation

Date Calibrated	8/2/2006	Analyst	TMG
Data File	1631 08-02-06	Reviewed	

Calibration Statistics			Calibration Blank Data			
STDEV CF	AVG CF	%RSD CF	AVG uABS	STDEV uABS	AVG Conc ng/L	STDEV ng/L
3.071	33.911	9.056	3.546	2.106	0.10	0.06
		PASS			PASS	PASS
	Limit =	<15% RSD		Limits =	<0.5 ng/L	< 0.1 ng/L

Standard	Conc, ng/L	uABS	CF	Conc	%Rec	
Blk-1	0	3.156		0.1		
Blk-2	0	5.820		0.2		
Blk-3	0	1.663		0.0		
STD-1	0.5	23.154	39.215	0.6	116	PASS
STD-2	5	160.167	31.324	4.6	92	
STD-3	25	834.285	33.230	24.5	98	
STD-4	50	1669.693	33.323	49.1	98	
STD-5	100	3250.091	32.465	95.7	96	
OPR-1	5		---	4.575	91.50	PASS
QCS	5	4	---	4.775	95.50	PASS
OPR-2	5	3	---	4.845	96.90	PASS

Microbac Laboratories, Inc.
Routine/Scheduled Maintenance Log
Instrument ID: CVAF-2

Month & Year: _____

Date	Minimum Frequencies												Comments				
	Daily					Weekly		Monthly		As Needed							
	PMT voltage	Reagent flows	Clean External Gold Trap	Gas pressure	High sid hf units	Waste	Check KMnO4 trap	Clean GLS	Check pump tubing	Clean fan filter	Check GLS tubing	Check autosamp. tubing		Change SnCl2 tubing	Change Hydroxyl tubing	Change rinse tubing	Change sample tubing
1																	
2																	
3																	
4																	
5																	
6																	
7																	
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SOP Revision Notification / Annual Review Form

SOP Name MERCURY USING AUTOMATIC FLUORESCENCE SPECTROSCOPY

☒ **New Revision** Old Revision # 1 New Revision # 2

Summary of changes: • Section 3.3: Removed the deviations from the reference method.

- Sec. 7.0: (1) Removed shoe covers from the supplies list; (2) Added Tackymat and new instruments to the supplies list.
- Sec 8.2: (1) Removed the specification that reagents must be stored in glass containers. (2) Reduced the preparation volume for Hydroxylamine Hydrochloride; (3) Removed the acid rinse solution; (4) Added 10% HCl Rinse and 10% HNO₃ rinse solutions.
- Sec 8.3: Updated the preparations of the Working Calibration Standard A, calibration standards, method blank, MSMSD, QCS Working Standard A, and QCS to reflect current lab practices.
- Sec 12.2: Added instructions for using the stannous and hydroxyl lines.
- Sec. 18.0: Added the maintenance log for the M8000.

By signing below, I certify that I have been *notified* about the approval of a *new revision* to the above mentioned SOP. I realize it is *my responsibility* to **read, understand and perform** the procedure as set forth in this new revision.

Initials & Date

Initials & Date

Initials & Date

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

☐ **Annual Review** Current Revision # _____

By signing below, I certify that I have **re-read, understand and agree to perform** the current revision of the above mentioned SOP.

Initials & Date

Initials & Date

Initials & Date

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Form revised 01/18/06

Appendix to Method 1631
Total Mercury in Tissue, Sludge, Sediment, and Soil
by Acid Digestion and BrCl Oxidation

Appendix to Method 1631
Total Mercury in Tissue, Sludge, Sediment, and Soil
by Acid Digestion and BrCl Oxidation¹

A1.0 Scope and Application

- A1.1 This Appendix provides two sample preparation (digestion) procedures for oxidation of total mercury (Hg) in solid and semi-solid sample matrices. These procedures may be used in conjunction with EPA Method 1631B: *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* for determination of mercury in tissue, sludge, sediment, soil, industrial samples, and certified reference materials.
- A1.2 The digestion procedures in this Appendix, in conjunction with Method 1631B, allow determination of Hg at concentrations ranging from 1.0 to 5000 ng/g in solid and semi-solid matrices. Higher concentrations can be measured by selection of a smaller sample size and/or dilution of the digestate.
- A1.3 The detection limit and minimum level of quantitation in this Method usually are dependent on the level of interferences rather than instrumental limitations. The method detection limit (MDL; 40 CFR 136, Appendix B) for Hg has been determined to be in the range of 0.24 to 0.48 ng/g when no interferences are present (see Appendix Tables A3 and A4). The minimum level of quantitation (ML) has been established as 1.0 ng/g. These levels assume a sample size of 0.5 g.
- A1.4 Because Hg concentrations in solids are typically 10^3 - 10^7 times higher than those found in aqueous samples, the sensitivity provided by the dual amalgam trap system and fluorescence detector described in Method 1631B may be more sensitive than necessary, and a single trap and/or cold vapor atomic absorption spectroscopy (CVAAS) instrument may be adequate. These modifications are allowed under the equivalency provisions in EPA Method 1631B. See Method 1631B Section 9.1.2. However, the dual amalgam trap system and fluorescence detector provide greater sensitivity and specificity in the presence of interferences, and this system must be used to overcome interferences, if present, and to achieve the sensitivity required, if necessary.

A2.0 Summary

- A2.1 Digestion I—This procedure is preferred for matrices containing organic materials, such as sludge and plant and animal tissues, because the organic matter is completely destroyed. In this procedure, a 0.2 - 1.5 g sample is digested with $\text{HNO}_3/\text{H}_2\text{SO}_4$. The digestate is diluted with BrCl solution to destroy the remaining organic material.
- A2.2 Digestion II—This procedure is preferred for geological materials because of rapid and complete dissolution of cinnabar (HgS), which is otherwise more slowly attacked by the BrCl in Digestion I. In this procedure, a 0.5 - 1.5 g sample is digested with aqua regia (HCl/HNO_3) to solubilize inorganic materials.
- A2.3 The Hg concentration in the digestate is determined using EPA Method 1631B.

¹ Based on a standard operating procedure provided by Frontier Geosciences, Inc.

A3.0 Definitions

See the Glossary at the end of Method 1631B for definitions of the terms used in this Appendix.

A4.0 Contamination and Interferences

- A4.1 For the complete recovery of mercury by Method 1631B, all Hg in the sample must be converted to Hg(II). This is accomplished by free halogens present in the digestion step.
- A4.2 In Digestion I, the addition of BrCl to the sample after it is fully solubilized $\text{HNO}_3/\text{H}_2\text{SO}_4$ is critical to convert methyl Hg to Hg(II). If the acid digestates are analyzed by Method 1631B without BrCl oxidation of tissues or geological media, a significant low bias may occur.
- A4.3 In Digestion II, the reaction between concentrated HCl and HNO_3 in aqua regia generates nitrosyl chloride (NOCl) and free Cl_2 , both of which are very strong oxidants for Hg-containing compounds including cinnabar (HgS) and precious metal amalgams that are not attacked by either acid alone. Aqua regia also converts all methyl Hg to Hg(II). The aqua regia procedure in Digestion II leaches but does not dissolve silicate minerals. Crustal elements such as Fe, Al, Cr, Ba, and Si may not be quantitatively recovered in some media using this procedure.
- A4.4 Digestates from both Digestion I and II contain free halogens and extreme caution must be taken to avoid purging these free halogens onto the gold sand traps (see Section 4.4.2 in Method 1631B). Introduction of free halogens may be avoided by analyzing an aliquot of the sample digestate smaller than 5 mL (Appendix Section A12.3), and by pipetting aliquots of the digestate into bubbler water already containing SnCl_2 . The use of hydroxylamine hydrochloride to remove free halogens (as prescribed in Method 1631B for aqueous samples) is not needed for solid sample digestates; there is a sufficient amount of SnCl_2 in the bubbler to reduce both Hg(II) and free halogens in digestate aliquots smaller than 5 mL.
- A4.5 If iodized coal or other elemental carbon samples are to be analyzed, the final acid concentration in the diluted sample must be greater than 40% (v/v), and all carbon particles must be settled prior to analysis to avoid re-adsorption of Hg on the carbon and an ensuing low bias.

A5.0 Safety

Observe the safety precautions in Method 1631B.

A6.0 Apparatus and Materials

- A6.1 Digestion vessel—50-mL borosilicate Erlenmeyer flask, calibrated to 40 ± 0.5 mL; or any other acid-cleaned, flat-bottomed, borosilicate glass container calibrated to 40 ± 0.5 mL.
- A6.2 Pressure release digestion cap—Clear glass sphere or inverted fluoropolymer cone, approximately 1.5 - 2.0 cm in diameter, initially cleaned by heating overnight in hot concentrated nitric acid. The sphere or cone acts as a pressure release valve during gas evolution. A common clear glass marble may be used as the sphere, or the cone may be custom manufactured. Colored glass marbles contain high levels of trace metals and must not be used. The cap must completely cover the opening of the digestion vessel without falling in, yet not be so large as to risk falling off when slightly lifted by the gas pressure in the vessel.

- A6.3 Electric hot plate—A temperature controlled electric hot-plate capable of maintaining a temperature of 100-110°C. A commonly available fluoropolymer-coated pancake griddle is excellent for this purpose. Do not use the griddle for heating flammable solvents.
- A6.4 Dilution vessels—Volumetric flasks, glass, 25, 50.0, and 100.0 mL, cleaned per the procedures in Method 1631B.
- A6.5 Digestate storage vessel—VOA vial, glass, 40-mL, with fluoropolymer-lined cap, cleaned per the procedures in Method 1631B, or purchase I-Chem level 300, trace metal clean, with fluoropolymer-lined cap, or equivalent.
- A6.6 Balance—Analytical, capable of weighing 1.0 mg.

A7.0 Reagents and Standards

A7.1 Reference matrices

- A7.1.1 Biota, including tissue and wet and dry municipal sludge—Chicken breast, skinless, boneless, purchased at a local supermarket, or other tissue demonstrated to be free of mercury at the MDL in Table A1.
- A7.1.2 Soil, sediment, and other geological samples—Playground sand or other sand-like material demonstrated to be free from mercury at the MDL in Table A1.
- A7.2 Nitric acid (concentrated)—Reagent grade, containing less than 5 pg/mL Hg. The HNO₃ must be pre-analyzed for Hg before use.
- A7.3 Sulfuric acid (concentrated)—Reagent grade, containing less than 5 pg/mL Hg. The H₂SO₄ must be pre-analyzed for Hg before use.
- A7.4 HNO₃/H₂SO₄ solution—In a fume hood, slowly add 300 mL of concentrated H₂SO₄ (Appendix Section A7.3) to 700 mL of concentrated HNO₃ (Appendix Section A7.2) in a fluoropolymer bottle.

Warning: This mixture gets hot and emits caustic fumes.

- A7.5 Dilute BrCl solutions—Use the concentrated (0.2N) BrCl solution in Section 7.6 of Method 1631B to produce the following solutions:
- A7.5.1 0.07 N bromine monochloride solution—Dilute 300 mL of 0.2N BrCl solution to 1000 mL with reagent water in a fluoropolymer bottle.
- A7.5.2 0.02 N bromine monochloride solution—Dilute 100 mL of concentrated BrCl solution to 1000 mL with reagent water in a fluoropolymer bottle.

A8.0 Sample Collection, Preservation, and Storage

- A8.1 Samples are collected into acid-cleaned glass, polyethylene, or fluoropolymer jars. For all except very low level and high water content samples, polyethylene bags are also acceptable. Dry solids

such as coal and ores may be collected and stored in heavy gauge paper pouches commonly used by geologists.

A8.2 Samples are collected using clean gloves. Equipment is rinsed between samples to avoid cross-contamination. In general, follow the sampling procedures in Method 1613B. The ultra-low level sampling procedures in EPA Method 1669 may not be necessary because Hg concentrations in solids are typically 10^3 - 10^7 times higher than those found in water samples.

A8.3 Sample shipment, storage, preservation, and holding times

A8.3.1 Dry samples—Samples such as ores, coal, paper, and wood may be shipped unrefrigerated and stored indefinitely in a cool, dry location known to have an atmosphere that is low in mercury.

A8.3.2 Biota samples—Samples containing biota, including wet and dry sludge, are shipped to the laboratory at 0-4 °C and may be processed and stored in one of the following two ways:

A8.3.2.1 Biota samples large enough to sub-sample are homogenized to a fine paste with a stainless steel mill, or finely chopped with stainless steel tools on an acid-cleaned, plastic cutting board. After homogenization, samples are stored frozen at < -15 °C in an acid-cleaned glass or fluoropolymer jar. The jar should be sized to be filled between 50 - 80% with sample. Samples may be stored frozen for a maximum of 1 year.

A8.3.2.2 If not analyzed upon receipt at the laboratory, biota samples may be lyophilized (freeze-dried) prior to homogenization and storage. Once lyophilized, biota samples may be stored unrefrigerated in a low-mercury atmosphere for a maximum of 1 year.

A8.3.3 Wet sediment samples—Wet sediment samples are chilled and shipped to the laboratory at 0-4 °C. Because freezing and thawing may adversely affect homogeneity by causing clumping and separation of the solids from the liquid, wet sediment samples must be aliquoted and weighed at the laboratory and prior to freezing if they are not analyzed upon receipt. Wet sediment samples may be held for 1 year if aliquoted, weighed, and frozen at < -15 °C. Sediment samples may be lyophilized and stored unrefrigerated for 1 year in a low-mercury atmosphere if only total Hg will be determined and no free elemental mercury (Hg^0) is expected to be in the samples.

A9.0 Quality Control

A9.1 The quality control (QC) measures in Section 9 of Method 1631B must be followed when analyzing samples using this Appendix. In addition, this Appendix requires method blanks. Descriptions of the modifications of the quality control measures in Method 1631B that are required for application to solid and semi-solid matrices are provided below.

A9.2 Initial demonstration of laboratory capability

- A9.2.1 Method detection limit (see Section 9.2.1 of Method 1631B)—The laboratory must achieve an MDL that is less than or equal to the MDL listed in Table A1.
- A9.2.2 Initial precision and recovery (IPR; see Section 9.2.2 of Method 1631B)—Analyze four aliquots of the appropriate reference matrix (see Appendix Section A7.1), each spiked with 4.0 ng of Hg. This amount will be 8 ng/g for a 0.5 g sample. Calculate the average percent recovery (X) and the RSD of percent recovery. Compare X and RSD with the corresponding IPR limits in Table A1. If X and RSD meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, RSD exceeds the precision limit or X is outside the recovery range, performance of the analytical system is unacceptable. Correct the problem and repeat the test.
- A9.3 Matrix spike/matrix spike duplicate (MS/MSD; see Section 9.3 of Method 1631B)
- 9.3.1 Spike and analyze 1 out of every 10 samples of the same matrix type, in duplicate, at a concentration 2 - 5 times the background concentration of Hg in the unspiked sample or at the concentration in the IPR (Appendix Section A9.2.2), whichever is greater. Calculate the percent recovery in each aliquot and the RPD between the aliquots. The individual recoveries and the RPD shall meet the MS/MSD recovery acceptance criteria in Table A1. If either recovery or the RPD does not meet the acceptance criteria, correct the problem and repeat the test according to the procedures in Sections 9.3.4 and/or 9.3.5 of Method 1631B.
- A9.4 Blanks (see Section 9.4 of Method 1631B)
- A9.4.1 Because of the high concentrations of mercury in solid samples, as compared to aqueous samples, field blanks (Section 9.4.3 of Method 1631B) and sampler check blanks (Section 9.4.4.2 of Method 1631B) are not required. However, it may be prudent to collect a sampler check blank the first time that a given set of sampling equipment is used and whenever it is suspected to be contaminated.
- A9.4.2 Method blank—For each batch of 20 samples (Section 9.1.7 of Method 1631B), digest and analyze a method blank using the most appropriate reference matrix (Appendix Section A7.1). The laboratory may process a greater number of method blanks, if desired, and average the results. The method blank must include all sample processing steps; e.g., homogenization (Appendix Section A8.3.2.1). The concentration of mercury in the method blank, or the average of multiple method blanks, must meet the QC acceptance criteria in Table A1; otherwise, the source of contamination must be eliminated and the batch reanalyzed.
- A9.5 Ongoing precision and recovery (OPR; see Section 9.5 of Method 1631B)—The OPR (laboratory control sample) for solid and semi-solid samples is test of the entire analytical system and includes all sample processing procedures; e.g., homogenization (Appendix Section A8.3.2.1) and digestion (Appendix Section A11.1 or A11.2).
- A9.5.1 Analyze an aliquot of the appropriate reference matrix (see Appendix Section A7.1), spiked at the concentration in the IPR (Appendix Section A9.2.2). Calculate the percent recovery.

- A9.5.2 Compare percent recovery with the OPR limit in Table A1. If percent recovery meets the acceptance criteria, system performance is acceptable and analysis of samples and blanks may continue. If, however, percent recovery is outside of the acceptance range, analytical system performance is unacceptable. Correct the problem and repeat the test according to Section 9.5.2 of Method 1631B.
- A9.6 Quality Control Sample (QCS) - Many certified reference materials (CRMs) are available for total mercury in plants, animals, fish, sediments, soils, and sludge. Recovery and precision for at least one QCS per batch of samples must meet the performance specifications provided by the supplier.
- A9.7 Replicate samples—Some samples, particularly sediments, may be heterogeneous. Replicates of these samples should be analyzed to characterize this heterogeneity. Replicate samples may also be required by a specific program to assess the precision of the sample collection, transportation, and storage techniques. The relative percent difference (RPD) between replicates should be less than 30%.

A10.0 Calibration and Standardization

- A10.1 Calibrate the CVAFS instrument system using the procedures in Section 10 of Method 1631B. The concentration of the calibration solutions is as given in Section 10.1.1.2 of Method 1631B. The amount of Hg in these solutions will be 0.05, 0.5, 2.5, 5.0, and 10.0 ng.
- A10.2 Calibration verification (VER)—Calibration of the CVAFS instrument system must be verified periodically using aqueous standards. In Method 1631B, the OPR is used for this verification because the standards are added to water (see Sections 10.2 and 9.5 of Method 1631B). In contrast, the OPR in this Appendix (Appendix Section A9.5) is used to demonstrate that the end-to-end analytical system remains in control. To avoid confusion, the periodic verification of calibration in this Appendix is referred to as "calibration verification" (VER). The VER is a spiked reagent water sample (an aqueous blank spike) and is used to determine that the CVAFS remains in control.
- A10.2.1 Prior to and after the analysis of 10 samples, verify calibration of the CVAFS instrument system using the OPR test in Sections 9.5.1 and 9.5.2 of Method 1631B. Record results as calibration verification (VER).
- A10.2.2 The requirements in Section 9.5.2 of Method 1631B must be met for sample results to be valid.

A11.0 Digestion

- A11.1 Digestion I: Hot re-fluxing $\text{HNO}_3/\text{H}_2\text{SO}_4$ digestion followed by BrCl oxidation—This procedure is intended for biota, wood, paper, tissue, municipal sludge, and other primarily organic matrices (excluding coal). It does, however, give quantitative recovery for Hg on finely divided geological matrices such as sediments and soils.
- A11.1.1 Accurately weigh (to the nearest mg) an aliquot of sample directly into a tared digestion vessel (Appendix Section A6.1). For organic matter such as biota, weigh 0.2-0.4 gram; for tissue (e.g., fish), plant material, or sludge, weigh 0.5-1.5 grams; for dried material

such as wood, paper, and CRMs, weigh 0.2-0.4 gram. The use of too much organic material will consume all of the acid in the digestion, resulting in a low recovery.

- A11.1.2 To each sample, add 10.0 mL of $\text{HNO}_3/\text{H}_2\text{SO}_4$ solution (Appendix Section A7.4). Place the digestion vessel in an acid fume hood and loosely cap with a clean marble or inverted fluoropolymer cone (Appendix Section A6.2). For wood, paper, or other dry carbohydrates that can react violently with the $\text{HNO}_3/\text{H}_2\text{SO}_4$ solution, allow the sample to sit in the cold acid for at least 4 hours before heating.
- A11.1.3 After digesting at room temperature, place the digestion vessel on a hot plate in the hood and slowly bring to a gentle boil by incrementally increasing the plate temperature over a 1-hour period. If excessive sample foaming occurs, bring to temperature more slowly. Reflux for 2-3 hours to fully oxidize remaining organic matter. The mineral portion of soil and sediment samples will not dissolve but will be effectively leached by this digestion.
- A11.1.4 After the digestion is complete, bring to the calibration mark on the digestion vessel (40 ± 0.5 mL; Appendix Section A6.1) with 0.02 N BrCl solution (Appendix Section A7.5.2) and mix thoroughly. Shake the sample/BrCl solution to homogenize, and allow to sit at least 4 hours prior to analysis to oxidize remaining dissolved methyl Hg. Analyze the oxidized digestate per Appendix Section A12.0.

Note: Some highly organic matrices will require higher levels of BrCl (Appendix Section A7.5.1) and longer digestion times or elevated temperatures. The amount of reagent added to a sample must be the same as the amount added to the reagent blank to detect contamination in the reagents, and to the method blank and the OPR to demonstrate that mercury can be recovered quantitatively. BrCl oxidation must be continued until it is complete.

- A11.2 Digestion II: Cold aqua regia followed by BrCl oxidation—This procedure is intended for coal, ores, sediments, soils, and other geological media. It does, however, give quantitative recovery for Hg on finely divided biological media such as tissues, paper, and wood, because the organic matrix is leached rather than dissolved. Solid, dry geological media such as rocks, ores, and coal must be pulverized using a contamination-free mill prior to digestion. Otherwise, mercury will not be recovered from the interior of large particles.
- A11.2.1 Accurately weigh (to the nearest mg) an aliquot of the sample directly into a tared digestion vessel. For wet sediments and soils, weigh 0.5-1.5 grams; for dried materials such as coal, ores, and CRMs, weigh 0.5-1.0 gram. To better assure homogeneity, sediments and soils should be screened through a 2-mm plastic sieve to remove large rocks and sticks before digestion.
- A11.2.2 In a fume hood, add 8.0 mL of concentrated HCl (Method 1631B Section 7.3), swirl, and add 2.0 mL of concentrated HNO_3 to the sample in the digestion vessel. Cap the vessel with a clean glass marble or inverted fluoropolymer cone. Allow to digest at room temperature for at least 4 hours but preferably overnight.
- A11.2.3 For coal or other elemental carbon-containing sample, dilute the digestate to the calibration mark (40 ± 0.5 mL) with 0.07 N BrCl solution and shake the flask to mix thoroughly. The addition of BrCl ensures that Hg will not re-adsorb to the carbon

particles, producing low recoveries. After dilution and shaking, allow the sample to settle overnight, or centrifuge prior to analysis. Be sure that all fine-grained particles are completely settled prior to analysis. This settling can be hastened by centrifuging for 20 minutes at 3000 RPM or by filtering the sample through a 0.45-mm filter. Analyze per Appendix Section A12.0.

A11.2.4 For other than coal or elemental carbon-containing samples, dilute the digestate to volume (40 ± 0.5 mL) with reagent water so that the meniscus is at the calibration line in the neck of the digestion vessel. Shake vigorously and allow settling until the supernatant is clear prior to analysis. Analyze per Appendix Section A12.0.

A11.3 The diluted digestates may be stored up to one year in glass or fluoropolymer containers prior to analysis, or for future re-analysis, if needed.

A12.0 Digestate Analysis

Diluted digestates are analyzed in a manner analogous to the analysis of standards by Method 1631B (see Section 10.0 of Method 1631B).

A12.1 Pipet a 0.01- to 5.0-mL volume of diluted digestate (Appendix Section A11.1.4, A11.2.3, or A11.2.4) directly into a bubbler containing approximately 100 mL of pre-purged SnCl_2 -containing water.

Note: The volume of SnCl_2 -containing water in the bubbler is not critical for the purpose of purging but is assumed to be 0.100 L for the purpose of calculating results (see Appendix Section A13.1.1).

A12.2 Purge the solution onto a gold trap for 20 minutes. These conditions allow measurement of Hg concentrations in the range of 1 – 5,000 ng/g (parts per billion).

A12.3 Change the SnCl_2 -containing water in the bubbler after a total of 10 mL of digestate has been added. For example, if 2 digestate aliquots of 5 mL each have been added to 100 mL of fresh, pre-purged, SnCl_2 -containing water, the SnCl_2 -containing water must be changed and 100 mL of fresh, SnCl_2 -containing water must be placed in the bubbler and purged for a minimum of 10 minutes prior to addition of another digestate aliquot.

A12.4 For samples known or expected to contain high Hg concentrations, further dilute (usually by a factor of 100) an aliquot of the diluted digestate with 0.02 N BrCl solution, and analyze a sub-aliquot.

A13.0 Data Analysis and Calculations

A13.1 Calculation of solid phase concentrations

A13.1.1 The analytical system in Method 1631B will give analytical results in units of area (or height) for the volume of diluted digestate analyzed. To calculate the solid phase concentration, use the following equation:

$$C_{\text{Hg}} = (A_s - A_{\text{BB}}) \times V \times d \times 0.1 / (CF_m \times v \times w)$$

where:

C_{Hg}	=	concentration of mercury in the sample (ng/g wet weight)
A_s	=	peak area (or height) for mercury in the sample
A_{BB}	=	peak area (or height) for the average of the bubbler blanks
V	=	volume of diluted digestate (mL) (Appendix Sections A11.1.4, A11.2.3, A11.2.4) = 40 mL
d	=	dilution factor(s); e.g., a factor of 100 in Appendix Section A12.4.
0.1	=	volume in bubbler (L) (Assumed per note in Appendix Section A12.1)
CF_m	=	mean CF from calibration (area (or height))/(ng/L) (Method 1613B Section 10.1.1.4)
v	=	digestate volume analyzed (mL) (Appendix Section A12.1)
w	=	sample weight (g) (Appendix Section A11.1.1 or A11.2.1)

A13.1.2 If desired, determine the moisture content of a sample aliquot and use the dry weight as “w” in the equation above.

A13.2 Reporting

A13.2.1 Report results as required in Method 1631B except use reporting levels and units appropriate to solid samples (ng/g).

A13.2.2 Reagent blank results and method blank results are reported separately and, if requested or required, are subtracted from sample Hg concentrations.

A14.0 Method Performance

A14.1 This Appendix was developed in a single laboratory and validated in a single laboratory. Performance data from these studies are summarized in Tables A2 through A7.

A15.0 References

1. *Development of Digestion Procedures for Determination of Mercury in Solid and Semi-solid Samples*, Frontier Geosciences, available from EPA Sample Control Center DynCorp I&ET, Alexandria, VA 22304 (703-461-2100; SCC@dyncorp.com).
2. *Single Laboratory Validation of Appendix to Method 1631*, June-July 1999, Brooks-Rand Ltd., EPA Sample Control Center Episode Number 6236, DynCorp I&ET, Alexandria, VA 22304 (703-461-2100; SCC@dyncorp.com).

Table A1. Quality control acceptance criteria.

Test	Acceptance Criteria	Spike concentration
Calibration linearity	<15% RSD of CF	0.5, 5, 25, 50, and 100 ng/L = 0.05, 0.5, 2.5, 5.0, and 10.0 ng
Calibration verification (VER)	77-123%	5 ng/L = 0.5 ng
MDL	0.48 ng/g ⁽¹⁾	0.8 ng/g
ML	1 ng/g ⁽²⁾	0.05 ng (lowest calibration point)
MS/MSD recovery	70-130%	2x background or level in IPR/OPR, whichever is greater
MS/MSD precision	< 30% RPD	2x background or level in IPR/OPR, whichever is greater
IPR recovery	75-125%	4.0 ng
IPR precision	< 20% RSD	4.0 ng
OPR recovery	70 - 130%	4.0 ng
Method blank	< 0.4 ng or < 0.1x sample, whichever is greater	-

(1) See Appendix Table A4

(2) Assuming a 0.5 g sample

Table A2. Method performance for biological samples and CRMs digested using hot re-fluxing HNO₃ digestion plus BrCl dilution and Method 1631B. Blanks and spikes were on three different instruments, over a period of several weeks. Data provided by Frontier Geosciences.

Test/material	n	Hg concentration (ng/g; ppb)			Performance
		mean	SD	certified ⁽¹⁾	
Method blanks	24	0.25	0.13	--	DL = 0.33 ng/g ⁽²⁾
2.0 ng/g matrix spike	28	1.90 ⁽³⁾	0.22	2.00	95% rec.; 11% RSD
IRM-007 (sludge)	3	3,680	150	3,150	117% rec.; 4% RSD
DOLT-2 (fish liver)	7	2,164	161	2,140	101% rec.; 7% RSD
DORM-2 (fish muscle)	11	4,682	386	4,640	101% rec.; 8% RSD
NIST-2796 (mussel)	12	60.4	6.7	61.0	99% rec.; 11% RSD

(1) value provided by supplier of reference material

(2) detection limit = 2.5 x SD for 24 method blanks (2.5 = student's t @ 23 degrees of freedom)

(3) net recovered; background concentration (chicken breast) was 0.41 ng/g

Table A3. Method performance for geological samples and CRMs using cold aqua regia digestion and Method 1631B. Data provided by Frontier Geosciences.

Test/material	n	Hg concentration (ng/g; ppb)			Performance
		mean	SD	certified ⁽¹⁾	
Method blanks	23	0.045	0.037	--	DL = 0.09 ng/g ⁽²⁾
0.5 ng/g blank spike	8	0.465	0.079	0.50	MDL = 0.24 ng/g
NIST-2709 (soil)	9	1393	111	1,400	100% rec.; 8% RSD
NIST-1633 (fly ash)	2	163	3.0	160	102% rec.; 2% RSD
NIST-2710 (soil)	3	30888	2,692	32,610	95% rec.; 9% RSD
IAEA-356 (sediment)	1	7152	--	7.62	94% rec.
PACS-1 (sediment)	1	4402	--	4,540	97% rec.
NIST-1630 (coal)	3	108	5.0	127*	85% rec.; 5% RSD
NIST-1632 (coal)	5	79.3	7.0	78	102% rec.; 9% RSD

(1) value provided by supplier of reference material

(2) detection limit = 2.5 x SD for 24 method blanks (2.5 = student's t @ 23 degrees of freedom)

Table A4. Results of MDL Set 2 analyses (spiked with 0.24 ng; ~0.8 ng/g). Data provided by Brooks-Rand.

Rep	Sample Mass (g)	Measured Hg (ng)	Blank-corrected Hg (ng)	Sample Concentration (ng/g)*
1	1.03	0.39	0.13	0.41
2	1.29	0.50	0.23	0.71
3	1.25	0.48	0.22	0.73
4	1.36	0.53	0.26	0.78
5	1.28	0.49	0.23	0.68
6	1.01	0.39	0.12	0.40
7	1.17	0.45	0.19	0.61
*blank corrected				Average: 0.62 ng/g Std. Dev.: 0.15 ng/g
				MDL = 0.48

Table A5. Analyses of spiked catfish samples (spiked with 17 ng of Hg). Data provided by Brooks-Rand

Replicate	Sample Mass (g)	Measured Hg (ng)	Recovered Hg (ng)*	%Recovery*
1	1.02	30.1	17.1	99.3
2	1.21	31.6	16.2	93.7
3	0.97	31.4	19.0	110.2
4	1.17	23.4	8.41	48.7
*background corrected				Average: 88% Std. Dev.: 27%

Table A6. Analyses of spiked powdered egg yolk (spiked with 2.9 ng of Hg). Data provided by Brooks-Rand.

Replicate	Sample Mass (g)	Measured Hg (ng)	Recovered Hg* (ng)	%Recovery
1	1.00	3.49	2.34	80.6
2	1.06	3.16	1.94	67
3	1.04	2.56	1.37	47.1
4	1.08	3.75	2.50	86.2
*background corrected				Average: 70% Std. Dev.: 17%

Appendix N
Laboratory SOPs

Microbac SOP
Methyl Mercury Draft, Revision 0

Total and Dissolved Methyl Mercury
By EPA 1630

**STANDARD OPERATING PROCEDURE FOR
METHYL MERCURY IN WATER
USING DISTILLATION, AQUEOUS ETHYLATION,
PURGE AND TRAP, AND CVAFS**

Revision Author: Matthew Sheehy

This SOP is effective upon signed approval by the following:

Metals Supervisor

Date

Quality Assurance Director

Date

DISCLAIMER: This SOP has been developed for use at the Microbac Laboratories, Merrillville, Indiana facility. It is intended for use by trained analysts. As written, this SOP may not be specifically applicable to the activities of other organizations.

Last Review Date:

No Changes Needed

Approved By:

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2.0 SCOPE AND APPLICATION

- 2.1 This procedure uses distillation, aqueous ethylation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS) for the determination of methyl mercury (CH_3Hg). This procedure is applicable to the analysis of aqueous samples. The applicable analytes, detection limits and routine reporting limits (PQL) are listed at the Limits tab of the applicable test codes in LIMS.

3.0 SUMMARY

- 3.1 A 100-2000 mL sample is collected directly into specially cleaned, pretested, fluoropolymer or borosilicate bottle(s) using sample handling techniques specially designed for collection of metals at trace levels (Reference 6).
- 3.2 For dissolved CH_3Hg , samples are filtered through a 0.45- μm capsule filter.
- 3.3 Fresh water samples are preserved by adding 4 mL/L of pretested 11.6 M HCl, while saline samples ($[\text{Cl}^-] > 500 \text{ ppm}$) are preserved with 2 mL/L of 9 M H_2SO_4 solution, to avoid distillation interferences caused by excess chloride.
- 3.4 Prior to analysis, a 45 mL sample aliquot is placed in a specially designed fluoropolymer distillation vessel, and 35 mL of the water is distilled into the receiving vessel at 125°C under N_2 flow.
- 3.5 After distillation, the sample is adjusted to pH 4.9 with an acetate buffer and ethylated in a closed purge vessel by the addition of sodium tetraethyl borate (NaBEt_4).
- 3.6 The ethyl analog of CH_3Hg , methylethyl mercury ($\text{CH}_3\text{CH}_2\text{CH}_2\text{Hg}$), is separated from solution by purging with N_2 onto a graphitic carbon (Carbotrap®) trap.
- 3.7 The trapped methylethyl mercury is thermally desorbed from the Carbotrap® trap into an inert gas stream that carries the released methylethyl mercury first through a pyrolytic decomposition column, which converts organo mercury forms to elemental mercury (Hg), and then into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection.
- 3.8 This procedure is based on the reference methods listed in section 17 of this document. This procedure contains no significant deviations {the following deviations} from the reference methods.

4.0 DEFINITIONS

- 4.1 A list of definitions is in the Quality Assurance Plan. In addition to the terms defined in the QAP, the terms below, if any, are specific and critical to this procedure.
- 4.2 Ambient Water – Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

- 4.3 Apparatus – Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis that come in contact with the sample and therefore require careful cleaning will be referred to collectively as the Apparatus.
- 4.4 Dissolved methyl mercury – All distillable CH_3Hg forms and species found in the filtrate of an aqueous solution that has been filtered through a 0.45 micron filter.
- 4.5 Intercomparison Study – An exercise in which samples are prepared and split by a reference laboratory, then analyzed by one or more testing laboratories and the reference laboratory. The intercomparison, with a reputable laboratory as the reference laboratory, serves as the best test of the precision and accuracy of the analyses at natural environmental levels.
- 4.6 Methyl mercury – All acid-distillable Hg, which, upon reaction with NaBEt_4 yields methylethyl mercury. This includes, but is not limited to, CH_3Hg^+ , strongly organo-complexed CH_3Hg compounds, adsorbed particulate CH_3Hg , and CH_3Hg bound in microorganisms. In freshly collected samples, dimethyl mercury ($(\text{CH}_3)_2\text{Hg}$) will not be recovered as CH_3Hg , but in samples which have been acidified for several days, most $(\text{CH}_3)_2\text{Hg}$ has broken down to CH_3Hg . In this method, CH_3Hg and total recoverable CH_3Hg are synonymous.
- 4.7 May – This action, activity, or procedural step is allowed but not required.
- 4.8 May not – This action, activity, or procedural step is prohibited.
- 4.9 Minimum Level (ML) – The lowest level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The ML is calculated by multiplying the MDL by 3.18 and rounding the result to the number nearest to $(1, 2, \text{ or } 5) \times 10^n$, where n is an integer.
- 4.10 Must – This action, activity, or procedural step is required.
- 4.11 Quality Control Sample (QCS) – A sample containing CH_3Hg at known concentrations. The QCS is obtained from a source external to the laboratory, or is prepared from a source of standards different from the source of calibration standards. It is used as an independent check of instrument calibration.
- 4.12 Reagent Water – Prepared from 18 MS ultrapure deionized water starting from a prepurified source. Reagent water is used to wash bottles, as source water for trip and field blanks, and in the preparation of standards and reagents.
- 4.13 Sample set – Samples collected from the same site or, if for compliance monitoring, from a given discharge. This term applies to samples collected at the same time, to a maximum of ten samples.
- 4.14 Shall – This action, activity, or procedure is required.

- 4.15 Should – This action, activity, or procedure is suggested, but not required.
- 4.16 Stock Solution – A solution containing an analyte that is prepared from a reference material traceable to EPA, NIST, or a source that will attest to the purity and authenticity of the reference material.
- 4.17 Ultraclean Handling – A series of established procedures designed to ensure that samples are not contaminated for CH₃Hg during sample collection, storage, or analysis.

5.0 **INTERFERENCES**

- 5.1 Preventing ambient water samples from becoming contaminated during the sampling and analysis process constitutes one of the greatest difficulties encountered in trace metals determinations. Over the last two decades, marine chemists have come to recognize that much of the historical data on the concentrations of dissolved trace metals in seawater are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels. Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.
- 5.2 Potential sources of trace metal contamination include:
- 5.2.1 *Metallic or metal-containing labware* (e.g., talc gloves that contain high levels of zinc), containers, sampling equipment, reagents, and reagent water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust.
- 5.2.2 *Human contact* can be a source of trace metal contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation.
- 5.2.3 *Samples*—Significant laboratory or instrument contamination may result when untreated effluents, in-process waters, landfill leachates, and other samples containing high concentrations of Hg or CH₃Hg are processed and analyzed. This method is not intended for application to these samples, and samples containing high concentrations of trace metals should not be permitted into the clean room and laboratory dedicated for processing trace metals samples.
- 5.2.4 *Carryover*—Contamination may occur when a sample containing a low concentration of CH₃Hg is processed immediately after a sample containing a relatively high concentration. When an unusually concentrated sample is encountered, an ethylation blank should be analyzed immediately following the sample to check for carryover. Samples known or suspected to contain the lowest concentration of CH₃Hg should be analyzed first followed by samples containing higher levels.

- 5.2.5 *Indirect contact*—Apparatus that may not directly come in contact with the samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in the collection, processing, and analysis of samples be thoroughly cleaned.
- 5.2.6 *Airborne particulate matter*—Airborne particles are less obvious substances capable of contaminating samples. Samples may be contaminated by airborne dust, dirt, particles, or vapors from unfiltered air supplies; nearby corroded or rusted pipes, wires, or other fixtures; or metal-containing paint. Whenever possible, sample processing and analysis should occur as far as possible from sources of airborne contamination.
- 5.2.7 *Hydrochloric acid* -- Distillation of CH_3Hg from solution requires a carefully controlled level of HCl in solution. Distillation will not be quantitative if too little HCl is added, but too much HCl results in co-distillation of HCl fumes, which interfere with the ethylation procedure. Therefore fresh water samples must be preserved only with between 0.3% and 0.5% (v/v) 11.6 M HCl, and salt water samples with between 0.1% and 0.2% (v/v) 9 M H_2SO_4 .
- 5.2.8 *Nitric acid* – Samples preserved with nitric acid (HNO_3) cannot be analyzed for CH_3Hg as the analyte is partially decomposed in the distillation step by this reagent.
- 5.2.9 *Carrier gas* -- The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause "quenching" of the excited atoms. The Carbotrap® trap eliminates quenching due to trace gases, but it still remains the analyst's responsibility to ensure high purity inert carrier gas and a leak-free analytical train. In some rare cases (such as oil polluted water) low molecular weight organic compounds may purge with the methylethyl mercury and collect on the Carbotrap® trap, subsequently resulting in signal quenching during elution. Such cases are best treated by sample dilution prior to distillation.
- 5.2.10 *High inorganic mercury concentrations* – Recent investigations have shown that a positive artifact is possible with the distillation procedure in cases where high inorganic Hg concentrations are present. In natural waters, approximately 0.01 to 0.05% of the ambient inorganic Hg in solution may be methylated by ambient organic matter during the distillation step. In most waters, where the percent CH_3Hg is 1-30% of the total, this effect is trivial. However, the analyst should be aware that in inorganic Hg contaminated waters, the fraction CH_3Hg can be <1% of the total, and so flagging of the data (as representing a maximum estimate of CH_3Hg concentration) may be warranted. In samples with high levels of divalent mercury (Hg(II)), solvent extraction may be preferable to distillation.
- 5.2.11 *Gold dust* – Great care should be taken to avoid contaminating the laboratory with gold dust. This could cause interferences with the analysis if gold becomes incorporated into the samples or equipment. The gilding procedure should be done in a remote laboratory if at all possible.

6.0 SAFETY

- 6.1 Consult the current revision of the Chemical Hygiene Plan. Requirements for the use of personal protective equipment (e.g. safety glasses, lab coats, gloves) as well as other area-specific safety requirements (e.g. gas cylinders) and MSDS sheets are addressed in the CHP.
- 6.2 Confinement—Isolated work areas posted with signs, segregated glassware and tools, and plastic absorbent paper on bench tops will aid in confining contamination.
- 6.3 Waste handling—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors and other personnel must be trained in the safe handling of waste.
- 6.4 Decontamination of personnel—Use any mild soap with plenty of scrubbing action.
- 6.5 Decontamination of glassware, tools, and surfaces—Activated carbon powder will adsorb CH₃Hg, eliminating the possible volatilization of CH₃Hg. Satisfactory cleaning may be accomplished by dusting a surface lightly with activated carbon powder, then washing with any detergent and water.
- 6.6 Laundry—Clothing known to be contaminated should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. If the launderer knows of the potential problem, the clothing may be put into a washer without contact. The washer should be run through a cycle before being used again for other clothing.
- 6.7 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by this method can achieve a limit of detection of less than 1 ng per wipe. Less than 0.1 µg per wipe indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe constitutes an acute hazard, requires prompt cleaning before further use of the equipment or work space, and indicates that unacceptable work practices have been employed.

7.0 EQUIPMENT AND SUPPLIES

The following is a list of materials needed to perform the steps of this procedure as written. See the reference method(s) for equipment and supply specifications.

- 7.1 All volumetric glassware used shall be ASTM Class A. Class B glassware must be verified for accuracy on an annual basis and labeled with an appropriate correction.
- 7.2 **Analytical balance** – capable of weighing to the nearest 0.01 g.
- 7.3 **Borosilicate or fluoropolymer glass sample collection bottles**, 125- to 1000 mL, with fluoropolymer or fluoropolymer-lined cap.

- 7.3.1 New bottles are cleaned by heating to 65-75°C in 4 N HCl for at least 48 h. The bottles are cooled, rinsed three times with reagent water, and filled with reagent water containing 1% HCl. These bottles are capped and placed in a clean oven at 60-70°C overnight. After cooling, they are rinsed three more times with reagent water, filled with reagent water containing 0.4% (v/v) HCl, capped, and placed in a mercury-free class 100 clean bench until the outside of the bottle is dry. The caps are then tightened with a wrench and the bottles are double-bagged in new polyethylene zip-type bags. The capped bottles are stored in wooden or plastic boxes until use.
- 7.3.2 To avoid long-term accumulation of Hg or CH₃Hg on the bottle walls due to trace organic coatings, used bottles are filled with reagent water containing 0.02 N BrCl solution and allowed to stand over night. The BrCl is neutralized with the addition of 0.2 mL of 20% NH₂OH solution. The bottles are then cleaned exactly as in the previous section, except that they soak only 6-12 h in hot 4 N HCl.
- 7.3.3 Bottle blanks should be analyzed to verify the effectiveness of the cleaning procedures.
- 7.4 **Cold vapor atomic fluorescence spectrometer (CVAFS)** – The system must consist of the following:
- 7.4.1 Low-pressure 4-W mercury vapor lamp
- 7.4.2 Far UV quartz flow-through fluorescence cell—12 mm x 12 mm x 45 mm, with a 10-mm path length (NSG Cells, or equivalent).
- 7.4.3 UV-visible photomultiplier (PMT)—sensitive to < 230 nm. This PMT is isolated from outside light with a 253.7-nm interference filter (Oriel Corp., or equivalent).
- 7.4.4 Photometer and PMT power supply (Oriel Corp., or equivalent), to convert PMT output (nanoamp) to millivolts.
- 7.4.5 Black anodized aluminum optical block—holds fluorescence cell, PMT, and light source at perpendicular angles, and provides collimation of incident and fluorescent beams (Frontier Geosciences Inc., or equivalent).
- 7.4.6 Flowmeter, with needle valve capable of keeping the carrier gas at a reproducible flow rate of 30 mL/min
- 7.4.7 Ultra high-purity argon (grade 5.0)
- 7.5 **Distillation unit** – The distillation unit is a custom made temperature controlled aluminum block heater, as shown schematically in Figure 3 (Frontier Geosciences Inc., or equivalent).
- 7.5.1 Heating block insulation – Each heating block is encased first in refractory spun rock insulation (1 inch thickness) and then an exterior wood shell for rigidity.

- 7.5.2 Each heating block (10 cm wide x 20 cm long x 15 cm high) is bored with five 31 mm diameter holes (evenly spaced), 120 mm deep. A 3/8 inch diameter hole is bored to 90% of the block length, perpendicular to and behind the distillation tube holes, to accommodate a cylindrical heating element. A 2 mm diameter hole is bored parallel to the heating element hole, and 2 cm above it, to accommodate the temperature sensor.
- 7.5.3 Heating element—Each heating block is equipped with a 750 watt cylindrical heating element, 6 inches long by 3/8 inch diameter (Omega Inc.), immobilized in its respective hole by a dab of silicone glue.
- 7.5.4 Type J thermocouple probe—Each heating block is equipped with a type J thermocouple probe immobilized in its respective hole by a dab of silicone glue.
- 7.5.5 Digital temperature controller—The heating element and thermocouple are connected to a digital temperature controller.
- 7.5.6 Fluoropolymer vials with caps—The distillation unit is designed to accommodate 60 mL fluoropolymer vials (part number 0202, Savillex, or equivalent). The original caps are used to close the vials when distillate is to be stored until analysis.
- 7.5.6.1 For each distillation, two identical vials are needed: a distillation vessel and a receiving vessel. For convenience, each vial should be engraved with a line at 40.0 mL (obtained by weighing 40 g of water in the vial), and a unique identification number, both on the vial and the cap.
- 7.5.6.2 Fluoropolymer vials are acid cleaned initially as described for other fluoropolymer ware and stored filled with 0.5% HCl. After use, receiving vials are rinsed with reagent water and filled with 0.5% HCL. The tubing is looped around the cap as described in Section 6.7.7.1, and the vials are placed in a 70°C ($\pm 5^\circ\text{C}$) oven overnight. Cleaning is the same for the distillation vials, with the exception that first the vials, caps, and tubing are thoroughly scrubbed with an alkaline detergent and test tube brush to remove any residues from the samples.
- 7.5.7 Purge caps—The standard caps on the fluoropolymer vials are replaced with purge caps for distillation purposes.
- 7.5.7.1 Fluoropolymer tubing—each purge cap is threaded with a piece of 1/8 inch fluoropolymer tubing, approximately 30-40 cm long. One end is pulled through one of the holes in the cap, down to a length that will allow it to reach the bottom of the distillation vial when the vial is screwed onto the cap. The bottom end of this tubing is cut at a 45° angle. The outside end of the tubing is cut perpendicularly and is looped around and inserted into the second cap hole when not in use (to keep the system closed and clean).
- 7.5.8 Aluminum distillation cover—The cover for the heating block consists of a 5 cm high aluminum block of the same cross section as the heating block (10

cm wide x 20 cm long), which has been milled out completely except for a 0.5 cm shell all around. In this lid is placed a series of 5 slots, 0.5 cm wide by 3 cm high, on each of the long sides, to allow passage of the distillation tubing in and out of the distillation vessels. **NOTE:** *It is very important that the heating block have an aluminum top covering the vessels, to avoid condensation and refluxing of the sample in the distillation vessels.*

- 7.5.9 Polyethylene container—Distillate is received and cooled in a fluoropolymer receiving vial supported in an ice bath in a polyethylene container. A box approximately 15 cm wide x 25 cm long x 10 cm high is a convenient container, and holes to accommodate the receiving vials can be cut into the lid of each box. Suitable boxes are generally available at sundries stores as storage containers.
- 7.5.10 Rotometer/needle valve—Five needle valve/rotometer (0-300 mL/min N₂) assemblies are required, one for each distillation vessel in the heating block. These rotometers can be mounted in banks of 5 for each distillation block, with all rotometers connected to a common gas manifold.
- 7.5.10.1 Fluoropolymer tubing—Inert gas (N₂ or Ar at 0.5-1 atm) is brought from the regulator to the manifold and from the rotometer outlets to the distillation vials by 1/8 inch fluoropolymer tubing.
- 7.5.11 The entire distillation set-up can be mounted on a stepped structure or shelving unit, such that the banks of rotometers are on the top and easily adjustable. Below the rotometers are the distillation blocks, and lower still, the ice baths for the receiving vessels.
- 7.6 **Filter**—0.45- μ m, 15-mm diameter capsule filter (Gelman Supor 12175, or equivalent)
- 7.7 **Isothermal gas chromatography (GC) system:**
- 7.7.1 Carbotrap® traps—10-cm x 6.5-mm o.d. x 4-mm i.d. quartz tubing. The tube is filled with 3.4 cm of 30/45 mesh Carbotrap® graphitic carbon adsorbant (Supelco, Inc., or equivalent). The ends are plugged with silanized glass wool. At least six are needed.
- 7.7.1.1 Traps are fitted with 6.5-mm i.d. fluoropolymer friction-fit sleeves for making connection to the system. When traps are not in use, fluoropolymer end plugs are inserted in trap ends to eliminate contamination.
- 7.7.1.2 Because the direction of flow is important in this analysis, the crimped end of the Carbotrap® trap will be referred to as “side A,” while the uncrimped end will be referred to as “side B.”
- 7.7.1.3 Heating of Carbotrap® traps—To desorb CH₃Hg collected on a trap, heat for 45 sec to 450-500EC (a barely visible red glow when the room is darkened) with a coil consisting of 75 cm of 24-gauge Nichrome wire at a

potential of 16-20 vac. Potential is applied and finely adjusted with an autotransformer.

- 7.7.2 Timer—The heating interval is controlled by a timer-activated 120-V outlet, into which the heating coil autotransformer is plugged.
- 7.7.3 Isothermal GC—Consists of two parts, a custom fabricated packed GC column, and a custom fabricated constant temperature oven.
- 7.7.3.1 The column is 1 m long, made from 0.25 inch OD by 4 mm ID borosilicate glass GC column tubing. The column is formed into an 8 cm diameter coil, with 15 cm straight extensions from each end. The column is silanized, packed in the coiled portion with 60/80 mesh 15% OV-3 on acid-washed Chromasorb W, and then conditioned under inert gas flow at 200°C. A column meeting these specifications may be custom fabricated (Supelco Inc., or equivalent).
- 7.7.3.2 The GC oven consists of a 500-watt aluminum jacketed heating mantle, fitted with a custom machined fluoropolymer lid (14 cm OD by 1 cm thick). The lid is attached with stainless steel screws and contains three threaded holes (0.25 inch female NPT) in a triangular pattern in the top. The spacing of the holes conforms exactly to the spacing between the two 15 cm glass extensions of the GC column.
- 7.7.3.3 Fluoropolymer fittings, with 0.25-inch male NPT threads on the bottom and 0.25-inch compression fittings on top, are placed into the threaded holes. The GC column is secured into the oven by passing the glass extensions through two of the fluoropolymer fittings, so that 3 cm of the glass extensions protrude from the top, and tightening the compression fittings. The fluoropolymer lid holding the GC column is then screwed to the top of the oven.
- 7.7.3.4 Temperature feedback control ($110 \pm 2^{\circ}\text{C}$) is achieved through a thermocouple temperature controller. The oven is plugged into the controller and the thermocouple probe is inserted through the third fluoropolymer fitting in the lid, such that the sensor is located near the center of the GC coil.
- 7.7.3.5 Several research groups have successfully interfaced the Carbotrap®/CVAFS system directly to a commercial gas chromatograph. The use of capillary column GC will result in better peak separation, although at higher cost.
- 7.7.4 Pyrolytic column—The output from the GC oven is connected directly to a high temperature column to decompose eluted organo-mercurial compounds to Hg_0 . The output of the pyrolytic column is connected to the inlet of the CVAFS system.
- 7.7.4.1 The column consists of a 20-cm length of quartz tubing, packed over the central 10 cm with quartz wool.

- 7.7.4.2 The column is heated to orange heat (~ 700°C) by a 1 m length of 22 gauge Nichrome wire, tightly wrapped around the quartz wool packed portion of the tube. The temperature of the coil is adjusted by visual inspection of the color, using a 0-120 volt autotransformer.

7.8 Methyl mercury purging system

- 7.8.1 Flow meter/needle valve—capable of controlling and measuring gas flow rate to the purge vessel at 350 (\pm 50) mL/min.
- 7.8.2 Fluoropolymer fittings—connections between components and columns are made using 6.4-mm o.d. fluoropolymer tubing and fluoropolymer friction-fit or threaded tubing connectors. Connections between components requiring mobility are made with 3.2-mm o.d. fluoropolymer tubing because of its greater flexibility.
- 7.8.3 Cold vapor generator (bubbler)—200 mL borosilicate glass (15 cm high x 5.0 cm diameter) with standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit that extends to within 0.2 cm of the bubbler bottom (Frontier Geosciences, Inc., or equivalent).
- 7.9 **Oven**, stainless steel, in class 100 clean area, capable of maintaining \pm 5°C in the 60-70°C temperature range.
- 7.10 **Panel immersion heater**, 500-W, all-fluoropolymer coated, 120 vac (Cole Parmer H-03053-04, or equivalent)
- 7.11 **Peristaltic pump**—115-V a.c., 12-V d.c., internal battery, variable-speed, single-head (Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent)
- 7.12 **Pipettors**—All-plastic pneumatic fixed-volume and variable pipettors in the range of 10- μ L to 5.0 mL.
- 7.13 **Recorder**—Any multi-range millivolt chart recorder or integrator with a range compatible with the CVAFS is acceptable. By using a two pen recorder with pen sensitivity offset by a factor of 10, the dynamic range of the system is extended to 10^3 .
- 7.14 **Tubing**—styrene/ethylene/butylene/silicone (SEBS) resin for use with peristaltic pump, approx 3/8-in i.d. by approximately 3 ft (Cole-Parmer size 18, Catalog No. G-06464-18, or approximately 1/4-in i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent).
- 7.14.1 Tubing is cleaned by soaking in 5-10% HCl solution for 8-24 h. It is rinsed with reagent water on a clean bench in a clean room and dried on the clean bench by purging with metal-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.
- 7.15 **Vat**: 100-200L, HDPE

7.15.1 The vat is half filled with 4N HCl in reagent water.

8.0 **REAGENTS AND STANDARDS**

8.1 All reagents used must be analytical reagent (AR) grade or higher. All standards must be traceable to NIST, when available. Certificates of traceability must be obtained from the manufacturer. All reagents and standards must be documented in the appropriate preparation logbook. Refer to the requirements in the Labeling of Standards, Reagents, Digestates and Extracts SOP.

8.2 Reagents

All stock reagents are stored in the Metals Cooler unless otherwise noted. Unless otherwise noted, prepared reagents are stored in {container type and location}, and prepared on an as needed basis.

8.2.1 Lab pure water (DI water): Analyte free water is prepared as described in the Quality Assurance Plan. DI water may be obtained from any of the designated taps throughout the lab. Reagent water—18-MΩ minimum, ultrapure deionized water starting from a prepurified (distilled, reverse osmosis, etc.) source. Water should be monitored for Hg, especially after ion exchange beds are changed.

8.2.2 Air—It is very important that the laboratory air be low in both particulate and gaseous Hg. Ideally, Hg work should be conducted in a new laboratory with mercury-free paint on the walls. Outside air, which is very low in Hg, should be brought directly into the class 100 clean bench air intake. If this is impossible, air coming into the clean bench can be cleaned for Hg by placing a gold-coated cloth prefilter over the intake.

8.2.2.1 Gold-coated cloth filter: Soak 2 m² of cotton gauze in 500 mL of 2% gold chloride solution at pH 7. In a hood, add 100 mL of 30% NH₂OH·HCl solution, and homogenize into the cloth with gloved hands. The material will turn black as colloidal gold is precipitated. Allow the mixture to set for several hours, then rinse with copious amounts of reagent water. Squeeze-dry the rinsed cloth, and spread flat on newspapers to air-dry. When dry, fold and place over the intake prefilter of the laminar flow hood.

8.2.3 APDC solution, 1% -- To 100 mL of reagent water, add 1.0 g of reagent grade APDC (ammonium pyrrolidine dithiocarbamate), and shake to dissolve. The solution is purified by extraction with three 10 mL aliquots of methylene chloride.

8.2.4 Acetate buffer, 2M – 2 moles of reagent grade sodium acetate (272 g) and 2 moles of reagent grade glacial acetic acid (118 mL) dissolved in reagent water to give a final volume of 1.0 L. To purify the buffer of traces of CH₃Hg, add 0.5 mL of 1% NaBEt₄ and purge the solution overnight with Hg-free N₂ or Ar. This solution has an indefinite lifetime when stored in a fluoropolymer bottle at room temperature.

8.2.5 Glacial acetic acid—Reagent grade Source:

- 8.2.6 Hydrochloric acid—Trace-metal purified reagent HCl containing less than 5 pg/mL Hg. CH₃Hg is not stable in concentrated acid, so the acid does not need to be tested for CH₃Hg. Source:
- 8.2.7 Methyl mercuric chloride(s)—A 5-g bottle of methyl mercuric chloride (s), reagent grade (Strem Chemical, or equivalent). Source:
- 8.2.8 Sodium tetraethyl borate, 1% – This reagent is purchased in 1.0-g air-sealed bottles.
- 8.2.8.1 One hundred milliliters of 2% KOH in reagent water is prepared in a fluoropolymer bottle and chilled to 0°C. The bottle of NaBEt₄ is rapidly opened and approximately 5 mL of the KOH solution poured in. The reagent bottle is capped and shaken to dissolve the NaBEt₄. This is poured into the 100 mL bottle of KOH solution, and shaken to mix. Immediately, the 1% NaBEt₄ solution in 2% KOH is poured into fifteen 7 mL fluoropolymer bottles, which are capped and placed in a low temperature freezer. For use, one of these bottles is removed and thawed until it starts to form a liquid layer. The reagent is then used until just before all of the ice is melted. Usually this lasts about 3 h if the bottle is placed in the refrigerator between uses.
- 8.2.8.2 *It is imperative that this reagent be exposed to air a minimum length of time. Thus, when removing reagent, open and close the lid quickly and tightly!* Frozen bottles of NaBEt₄ will keep for at least one week. Do not use NaBEt₄ solid or solutions if they have a yellow color.
- 8.2.8.3 NaBEt₄ is toxic, gives off toxic gases (triethylboron), and is spontaneously combustible. To discard unused portions of ethylating agent and empty bottles, place into a large beaker of 1N HCl in the hood. Triethylboron will bubble off to the air where it is eventually oxidized to harmless boric acid. Leave the acid beaker in the hood indefinitely, or boil down to 1/2 volume to destroy residues before discarding as any acid waste. (Strem Chemical, or equivalent) Source:
- 8.2.9 Sulfuric acid—Trace-metal purified reagent H₂SO₄ containing less than 5 pg/mL Hg. CH₃Hg is not stable in concentrated acid, so the acid does not need to be tested for CH₃Hg. Source:
- 8.2.10 IPR and OPR solutions—Using the working CH₃Hg standard prepare IPR and OPR solutions at a concentration of 0.5 ng/L as Hg in reagent water.
- 8.2.11 Nitrogen—Grade 4.5 (standard laboratory grade) nitrogen that has been further purified by the removal of Hg using a gold-coated sand trap.
- 8.2.12 Argon—Grade 5.0 (ultra high-purity, GC grade) that has been further purified by the removal of Hg using a gold-coated sand trap.
- 8.2.13 Gold-coated sand trap—The trap is made from 10-cm x 6.5-mm o.d. x 4-mm i.d. quartz tubing. The tube is filled with 3.4 cm of gold-coated 45/60 mesh quartz sand (Frontier Geosciences Inc., or equivalent). The ends are plugged

with quartz wool. Traps are fitted with 6.5-mm i.d. fluoropolymer friction-fit sleeves for connection to the system.

8.3 Standards

All stock standards are stored in the metals cooler unless otherwise noted. Unless otherwise noted, prepared standards are stored in {container type and location}, and prepared on an as needed basis.

8.3.1 Stock methyl mercury standard—Either procure certified CH_3Hg solution (Frontier Geosciences Inc., or equivalent) or prepare the stock solutions in the laboratory. Dissolve the contents of an entire 5-g bottle of methyl mercuric chloride in reagent water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl in a fluoropolymer bottle. This solution contains 4000-5000 mg/L CH_3Hg as Hg. It does not have a specific titre because, due to the contamination danger, the methyl mercuric chloride is not weighed. The stock solution has an indefinite lifetime when stored in an amber glass bottle with a fluoropolymer lid at room temperature. Do not make or keep this concentrated stock solution in the trace mercury laboratory.

8.3.2 **NOTE:** Making a CH_3Hg standard rather than purchasing one requires the laboratory to have available the technology to perform analyses with Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. Total Hg and labile Hg (II) determinations, made with Method 1631, are necessary to accurately determine the CH_3Hg concentration of the standards. Additionally, laboratories must be cautioned against assuming that purchased CH_3Hg stock solution will remain constant in concentration. Purchased stock solution has been seen to degrade occasionally, in one case from 1000 mg/L to 4 mg/L.

8.3.3 Secondary methyl mercury standard – Dilute 1.00 mL of stock solution (B) to 1000.0 mL with reagent water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl. This solution contains approximately 4-5 mg/L (5.00 ng/mL) CH_3Hg as Hg. The exact CH_3Hg titre is determined as indicated in Sections 7.11.1-7.11.4. The secondary CH_3Hg standard solution has been observed to maintain its titre over a year when stored in a fluoropolymer bottle in the refrigerator.

8.3.3.1 Dilute the secondary standard 1:10 with concentrated BrCl solution (0.100 mL of secondary stock solution added to 0.900 mL BrCl in a small FEP vial). Allow the solution to oxidize for at least 4 h. The total Hg in the dilution may then be analyzed using dual amalgamation/CVAFS, by comparison to a dilution of NIST-3133 (as in Method 1631). A mean of at least seven replicate analyses of the secondary stock solution is necessary to accurately quantify the total Hg concentration of the solution.

8.3.3.2 Analyze the secondary standard for labile Hg(II) using Method 1631 by directly reducing an aliquot of standard solution with SnCl_2 , but without

prior BrCl oxidation as performed in Section 7.11.1. At least two determinations of labile Hg(II) must be made of the stock solution.

- 8.3.3.3 Calculate the CH₃Hg in the secondary CH₃Hg standard solution by subtracting the mean labile Hg(II) concentration from the mean total Hg concentration.
- 8.3.3.4 If the secondary CH₃Hg stock solution drops below 98.0% CH₃Hg, discard the solution and make a fresh secondary solution.
- 8.3.4 Working methyl mercury standard—Prepare a dilution of the secondary CH₃Hg standard using reagent water containing 0.5% (v/v) glacial acetic acid and 0.2% (v/v) HCl. A convenient concentration for this standard is 1.00 ng/mL CH₃Hg as Hg. This solution will maintain its titre for more than one month when kept in a fluoropolymer bottle on the lab bench top. Refrigeration is not necessary

9.0 SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

- 9.1 The client or other trained personnel collect samples. Samples received at the laboratory are considered representative unless otherwise noted.
- 9.2 Samples should be collected in rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps. Preservation consists of adding 4 mL/L of concentrated HCl and storage in the range of 0.1-6°C. Saline samples ([Cl⁻] > 500 ppm) are preserved with 2 mL/L of 9 M H₂SO₄ solution.
 - 9.2.1 Samples may be shipped to the laboratory unpreserved if they are (1) collected in fluoropolymer bottles, (2) filled to the top with no head space, (3) capped tightly, (4) maintained at 0-4°C from the time of collection until preservation, and (5) preserved within 48 h of sampling.
- 9.3 Samples are stored in the {storage location}. Samples that fail to meet the preservation criteria are noted as such on the Cooler Inspection Report in the Login process.
 - 9.3.1 Borosilicate glass bottles may be used if Hg and Hg species are the only target analytes.
 - 9.3.2 It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads.
 - 9.3.3 Polyethylene sample bottles must not be used.
- 9.4 For dissolved CH₃Hg, samples and field blanks are filtered through a 0.45 µm capsule filter
- 9.5 Analysis must be performed within the maximum allowable hold time of 180 days from collection.

10.0 QUALITY CONTROL

- 10.1 An *Initial Demonstration of Capability* study must be performed prior to the initial analysis for each analyst and whenever substantial change has occurred in the procedure or instrument. Refer to the Capability and Detection Limit Studies SOP for details.
- 10.1.1 Four replicates of the IPR solution (0.5 ng/L) must be analyzed, their average percent recovery and standard deviation calculated, and meet the statistical standards for the method.
- 10.2 A *Method Detection Limit* study must be performed for each new procedure, annually thereafter, and whenever a change in instrument occurs. Refer to the Capability and Detection Limit Studies SOP for details.
- 10.2.1 To establish the ability to detect CH₃Hg, the analyst shall determine the MDL according to the procedure at 40 *CFR* 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL listed in Section 1.5 or one-third the regulatory compliance limit, whichever is greater. The MDL should be determined when a new operator begins work or whenever, in the judgment of the analyst, a change in instrument hardware or operating conditions would dictate that the MDL be redetermined.
- 10.3 {Identify the required QC parameters. Put QC test name in *italics*. List the frequency, acceptance limits, and corrective action if it fails. The effect on sample data and where/how the results of these QC tests are documented (e.g. CAR, data flag as defined in LIMS, etc.) must also be included. If statistical limits are used, include, "Details for the determination of statistical limits are in the Generation and Updating of Statistical Recovery Limits SOP". Put the QC parameters in their order of occurrence in a batch.}
- 10.4 A *Calibration Verification Standard* must be analyzed immediately after calibration, after every 10 samples, and after the last sample. The concentration of the ICV must be different than that of the CCV.
- 10.4.1 Acceptance criteria are the {statistical or nominal} limits listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.
- 10.4.2 ICV and CCV standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.
- 10.4.3 The reporting of data associated with a failed control sample must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.
- 10.4.4 Samples associated with a verification that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.

- 10.5 *A Calibration Verification Blank* sample must be analyzed after each calibration verification standard.
- 10.5.1 The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier. Samples for compliance with our Wisconsin DNR certification must be evaluated down to the current MDL and corrective action taken if the blank exceeds the routine PQL.
- 10.5.2 ICB and CCB standards that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier. ICB/CCB standards that are below the reporting limit but above the MDL are flagged in LIMS with a "b" qualifier. "b" flagged data is considered as meeting the acceptance criteria.
- 10.5.3 If the blank does not meet the acceptance criteria, all samples < PQL or greater than 10 times the blank contamination may be reported. All other environmental samples must be reanalyzed or reported with an appropriate qualifier in the Case Narrative of the report. The reporting of data associated with a failed control sample must be documented with a CAR form.
- 10.6 *A Method Blank* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per batch.
- 10.6.1 .
- 10.6.2 The method blank is prepared by the distillation of 45 mL aliquots of 0.4% HCl acidified reagent water, exactly as if they were samples.
- 10.6.3 The acceptance criteria are < PQL. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier. Samples for compliance with our Wisconsin DNR certification must be evaluated down to the current MDL and corrective action taken if the blank exceeds the routine PQL.
- 10.6.4 MBLKs that fail to meet the acceptance criteria cause the sample results to be automatically flagged in LIMS with a "B" qualifier. MBLKs that are below the reporting limit but above the MDL are flagged in LIMS with a "b" qualifier. "b" flagged data is considered as meeting the acceptance criteria.
- 10.6.5 The reporting of data associated with a failed control sample must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.
- 10.6.6 Samples associated with a MBLK that fails with positive bias can be reported without narration if the sample concentration is < PQL or greater than 10 times the blank contamination.

- 10.7 *A Laboratory Control Sample* must be prepared and analyzed with each batch of maximum 20 samples and at a minimum of one per day.
- 10.7.1 Acceptance criteria are the {statistical or nominal} limits listed in the appropriate test code in LIMS. If the acceptance criteria are not met, reanalyze. If reanalysis fails to meet the acceptance criteria, stop analysis and recalibrate or report data with an appropriate qualifier.
- 10.7.2 LCSs that fail to meet the acceptance criteria are automatically flagged in LIMS with a "S" qualifier.
- 10.7.3 The reporting of data associated with a failed LCS must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.
- 10.7.4 Samples associated with a LCS that fails with positive bias can be reported without narration if the sample concentration is below the reporting limit.
- 10.8 *A Matrix Spike and Matrix Spike Duplicate* sample must be prepared and analyzed with each batch of maximum 10 samples per matrix and at a minimum of one per day.
- 10.8.1 Acceptance criteria are the {statistical or nominal} limits listed in the appropriate test code in LIMS. (Note: the accuracy criteria have been met provided at least either the MS or MSD meet the %R criteria.) If the acceptance criteria are not met, refer to the MS/MSD Corrective Action Flowchart in the QAP.
- 10.8.2 MS/MSD's that fail to meet the accuracy criteria are automatically flagged in LIMS with a "S" qualifier. MSD's that fail to meet the precision criteria are automatically flagged in LIMS with a "R" qualifier.
- 10.8.3 The reporting of data associated with a failed MS/MSD must be documented with a CAR form. If the failure is considered to have a significant affect on the data, client notification is required using the Case Narrative of the report.
- 10.8.4 Samples associated with a MS/MSD that fails the accuracy criteria with positive bias can be reported without narration if the sample concentration is below the reporting limit.
- 10.8.5 If the concentration measured in the sample is greater than 4-times the concentration of the spike, the spike amount used is insufficient and the MS/MSD not applicable.
- 10.9 *An Ongoing Precision and Recovery (OPR)* sample must be prepared and analyzed with each batch of maximum 20 samples per matrix and at a minimum of one per day.
- 10.9.1 Analyze the OPR solution (0.5 ng/L, Section 7.10) followed by a ethylation blank prior to the analysis of each analytical batch. An OPR must also be analyzed at the end of an analytical run or at the end of each 12-hour shift.

Subtract the peak height (or peak area) of the ethylation blank from the peak height (or area) for the OPR and compute the concentration for the blank-subtracted OPR.

- 10.9.2 Compare the computed OPR concentration with the limits in Table 2. If the concentration is in the range specified, the analysis system is within specification and analysis of samples and blanks may proceed. If, however, the concentration is not in the specified range, the analytical process is not within the specified limits. Correct the problem and repeat the OPR test.
- 10.9.3 The laboratory should add results that pass the specification in Section 9.5.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (sr). Express the accuracy as a recovery interval from $R - 2sr$ to $R + 2sr$. For example, if $R = 95\%$ and $sr = 5\%$, the accuracy is 85-105%.
- 10.10 An *Quality Control sample (QCS)* sample must be prepared and analyzed with each batch of maximum 20 samples per matrix and at a minimum of one per day.
- 10.10.1 Quality control sample (QCS)—The laboratory must obtain a QCS from a source different from the CH_3Hg used to produce the standards used routinely in this method (Sections 7.7-7.10). The QCS should be analyzed as an independent check of instrument calibration in the middle of the analytical batch (e.g., for a batch of 14 samples, the QCS should be analyzed after the seventh sample). Good QCS samples may be made by KOH/methanol digestion (Reference 2) of CH_3Hg certified tissue CRMs.

11.0 **CALIBRATION AND STANDARDIZATION**

Calibration data is documented and retained using the {printouts from the instrument software or XXX raw data form (copy attached)}. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

- 11.1 {list frequency or criteria that require calibration/standardization. Note any requirements for the concentration of calibration standards. Note any documentation specifics such as naming conventions, location, etc. List the criteria for an acceptable calibration and the corrective action if these criteria are not met. Include "Analysis of environmental samples cannot proceed without the generation of an acceptable calibration."}
- 11.2 The analytical/toploading balance must be calibrated/verified in accordance with the Balance Calibration SOP.
- 11.3 The thermometers used must be verified in accordance with the Thermometer Calibration SOP.

- 11.4 The repipetters used must be verified in accordance with the Pipette Calibration SOP.
- 11.5 Perform the required preventative maintenance as necessary. Documentation is retained in the Maintenance Log for the particular instrument used for analysis.
- 11.6 A new calibration curve must be prepared annually. Verification of the curve is required prior to sample analysis each day of analysis. Analysis of environmental samples cannot proceed without the generation of an acceptable calibration.
- 11.7 ESTABLISHING A CALIBRATION CURVE

Establish the operating conditions necessary to purge Hg species from the bubbler and to desorb Hg species from the traps so that sharp peaks are given. The system is calibrated using CH₃Hg standards ultimately traceable to NIST standard total Hg reference material, as follows:

- 11.8 Calibration
- 11.8.1 The calibration must contain five or more non-zero points and the results of analysis of one ethylation blank. The lowest calibration point must be at the minimum level (ML).
- 11.8.2 Standards are analyzed by the addition of aliquots of the CH₃Hg working standard directly into the bubblers. Add 50 mL of fresh reagent water, a 0.005 ng aliquot of the standard, 0.3 mL of acetate buffer, and 0.04 mL of NaBEt₄ to the bubbler, swirling to mix.
- 11.8.3 Allow to react for 17 min, and then purge and analyze as below (Section 11). Sequentially follow with aliquots of 0.05, 0.1, 0.2, and 0.01 ng CH₃Hg in separate bubblers.
- 11.8.4 For each point, correct the standard peak height or area by subtracting the peak height or area of the ethylation blank for the analytical batch. Calculate the calibration factor (CF) for CH₃Hg for each of the five standards using the mean ethylation-blank-corrected peak height or area. (Equation 3).
- 11.8.5 Calculate the mean calibration factor (CF_m), the standard deviation of the CF_m (SD), and the relative standard deviation (RSD) of the calibration, where $RSD = 100 \times SD/CF_m$. If the RSD is $\leq 15\%$, the CF_m may be used to calculate sample concentrations. If $RSD > 15\%$, recalibrate the analytical system and repeat the test.
- 11.8.6 The net concentration recovery (minus ethylation blank) for the lowest standard must be in the range of 65-135% of the expected value to continue with sample analysis.
- 11.8.7 Ongoing precision and recovery—Perform the ongoing precision and recovery test to verify calibration prior to analysis of samples in each analytical batch. An OPR must also be analyzed at the end of an analytical run or at the end of each 12-hour shift.

- 11.8.8 Prepare the standards for the calibration curve as detailed in the Standards section of this SOP.

11.9 DAILY CALIBRATION

12.0 PROCEDURE

Analytical data is documented and retained using the {printouts from the instrument software or XXX raw data form (copy attached)}. Analytical data must be maintained in accordance with the document control requirements in the Quality Assurance Plan as well as the Document Control SOP.

12.1 Sample Distillation

- 12.1.1 Weigh a 45 mL aliquot from a thoroughly shaken, acidified sample, into a 60 mL fluoropolymer distillation vial. Add 200 μ L of 1% APDC solution, and replace the distillation cap, such that the tubing extends to the bottom of the vial.
- 12.1.1.1 Repeat this procedure for all samples to be distilled in a set, including three reagent water blanks and spiked samples.
- 12.1.1.2 Matrix spikes and matrix spike duplicates—For every 10 or fewer samples, pour two additional 45 mL aliquots from a randomly selected sample. Spike the aliquots at the level specified in Section 9.3 and process them in the same manner as the samples. There should be two MS/MSD pairs for each analytical batch of 20 samples.
- 12.1.1.3 For each sample, prepare a 60 mL distillate receiving vial. Add 5.0 mL reagent water to each receiving vial and replace the cap so that the tubing extends into the water layer.
- 12.1.1.4 Record the sample ID associated with each distillation and receiving vial. It is important to develop an unambiguous tracking system, such as the use of engraved vial numbers, because the distillation vials themselves cannot be labeled (due to the heat).
- 12.1.2 Place each prepared distillation vial into one of the holes in the heating block and attach the fluoropolymer tubing to the incoming gas supply from the rotometer manifold. Adjust the gas flow rate through the bubbler to 60 ± 20 mL/min.
- 12.1.3 As each distillation vial with sample is placed into the heating block, place the corresponding labeled distillation vial into the ice bath immediately adjacent to the heating block. Attach the tubing from the receiving vessel to the port of the distillation vessel.
- 12.1.4 Once all the holes in a heating block are filled, place the aluminum lid over the vessel caps in such a way that all tubing is passing without crimps through the slots, and the lid is making metal-to-metal contact with the block (to provide proper heating of the lid).

- 12.1.5 Turn on the temperature controllers to the heating blocks to a pre-set block temperature of $125 \pm 3^{\circ}\text{C}$.
- 12.1.6 Distill the samples until each receiving vial fills to the engraved 40 mL line. This time period will be approximately 2.5 h to 4 h depending upon exact temperatures, gas flow rates, and water characteristics.
- 12.1.6.1 Different samples and locations on the block will distill at somewhat different rates, so after about 2 h, all of the tubes should be monitored frequently to avoid over-distillation. As the individual samples fill to the line, they should be removed from the distillation unit.
- 12.1.6.2 Over-distillation is the greatest potential risk for poor recoveries by this method. If more than the prescribed amount of sample distills over, the risk of HCl fumes co-distilling increases. Chloride and low pH are interferences with the ethylation procedure.
- 12.1.6.3 If any samples are suspected of over-distillation, they should be checked with pH paper. If the distillate has a pH of less than 3.5, it should be discarded, rather than analyzed.
- 12.1.7 Once all of the vials are distilled, the distillates may be stored at room temperature and in the dark for up to 48 h before analysis (loop the fluoropolymer tube around to close off the second port on the receiving vial). Do not refrigerate or store longer than 48 h.
- 12.1.8 The distillation-side (dirty) vials must be scrubbed thoroughly with a test-tube brush and alkaline detergent, then rinsed in reagent water, to remove organics prior to acid cleaning. To acid-clean between uses, the vials are filled with 10% HCl, recapped with the tubing looped around to close off the port, and placed in an oven at 80°C overnight.
- 12.2 Ethylation and purging of the distillates
- 12.2.1 Immediately before analysis, add 0.3 mL of acetate buffer to the sample in the receiving vial, and then add another 10 mL of reagent water to the vial (so that the total sample volume is > 50 mL; the vial is almost full).
- 12.2.2 Pour the buffered sample into the reaction vessel/bubbler, and add 0.04 mL of freshly thawed 1% NaBEt_4 solution. Close the reaction vessel with the bubbler cap, and swirl gently to mix.
- 12.2.3 If standards, ethylation blanks, or QCS are being analyzed, pour 50 mL of reagent water into the bubbler, add 0.3 mL of acetate buffer, the appropriate spike, etc., and 0.04 mL 1% NaBEt_4 solution.
- 12.2.4 Allow the contents of the bubbler to react for 17 min. All CH_3Hg in the sample is converted to volatile methylethyl mercury.
- 12.2.5 After reaction, attach a Carbotrap® trap to each bubbler with the 1/4" fluoropolymer fitting, and purge the sample with N_2 (200 mL/min) for 17 min.

NOTE: The Carbotrap® trap must be attached such that the gas from the bubbler enters the trap on side A.

- 12.2.6 Once the sample has been purged for 17 min, any adsorbed water must be dried from the Carbotrap® trap. Disconnect the Carbotrap® trap from the bubbler and attach the N₂ flow directly to the trap. Use the same orientation (i.e., N₂ entering from side A), and purge the trap for 7 min.
- 12.2.7 The sample is now ready for analysis. The methylethyl mercury collected on the trap is quantitatively stable for up to 6 h and must be analyzed within that period.
- 12.3 Desorption of methylethyl mercury from the Carbotrap® trap
- 12.3.1 Close the argon stopcock on the GC, and allow 30 sec for the pressure in the system to dissipate. Remove the previous Carbotrap® trap from the GC.
- 12.3.2 Attach the Carbotrap® trap containing the new sample to the GC column using a 1/4" fluoropolymer friction fit connector, *such that side A is facing toward the GC column.*
- 12.3.3 Place the Nichrome wire heating coil around the Carbotrap® trap, centered over, and extending beyond the packing material on side A. Re-connect the argon gas to side B of the Carbotrap® trap.
- 12.3.4 Open the argon stopcock, and allow gas to flow for 30 sec prior to heating the column. Make sure that the post GC pyrolytic column is on and red-hot (~700°C).
- 12.3.5 Apply power to the coil around the sample trap for 45 sec (using an automatic timer) to thermally desorb the ethylated species from the sample trap into the GC column.
- 12.3.6 Turn on the chart recorder or other data acquisition device to start data collection.
- 12.3.7 Three peaks should emerge during the analytical run. The first peak (~1 min) is Hg₀, which is residual, and non-quantitative. This peak signifies the start of the peak set. Usually, the second peak to emerge (~2.5 min) is methylethyl mercury, the peak of interest. Following this (~4 min) is the peak for diethyl mercury ((CH₃CH₂)₂Hg), which is the ethylation product of Hg(II). If (CH₃)₂Hg were present in the sample, it would appear as a second peak between Hg₀ and methylethyl mercury-not fully resolved from the Hg₀. See appendix for advice on the quantitation of (CH₃)₂Hg.
- 12.3.8 Allow the GC run to proceed at least 1 min beyond the point that the diethyl mercury(Hg(II)) peak returns to base line. Place the next sample Carbotrap® trap in line and proceed with analysis of the next sample.
- 12.4 Peaks generated using this technique should be very sharp and almost symmetrical. Methylethyl mercury elutes at approximately 2.5 min and has a

width at half-height of about 10 sec. Earlier peaks (Hg_0 , $(\text{CH}_3)_2\text{Hg}$) are sharper, while later peaks (diethyl mercury) are broader.

- 12.4.1 The appearance of only one peak (Hg_0) usually signifies either that the pyrolytic column is not turned on, or that NaBEt_4 was not added to the sample.
- 12.4.2 Normally the Hg_0 peak is quite small. However, some Hg_0 is generated by thermal degradation of diethyl mercury during the desorption step. Thus, when samples contain a high concentration of Hg(II) , both the Hg_0 and the diethyl mercury peaks will be bigger. The ratio of the two peaks is indicative of the quality of the Carbotrap® trap. As the Carbotrap® trap degrades, the amount of thermal breakdown of organo-mercurials increases. Since the diethyl mercury is much more sensitive to thermal breakdown than the methylethyl mercury, monitoring the latter peak can serve as an early warning for Carbotrap® trap replacement. Generally, the Carbotrap® traps should be replaced any time the Hg_0 peak grows to be as large as the diethyl mercury peak. As a rule of thumb for samples with significant Hg(II) , use 1.0 ng Hg(II) from a non-acidified solution deliberately added to the reaction vessel as a trap check. For samples very low in Hg(II) , such as blanks, the Hg_0 peak is generally higher than the diethyl mercury peak, due to residual sources.
- 12.4.3 In the event that samples with large Hg(II) content are analyzed, some of the diethyl mercury generated breaks down to monoethyl mercury ($\text{CH}_3\text{CH}_2\text{Hg}$) during thermal desorption. If this occurs, a very broad peak (width of several minutes) will appear at some long time after the run is over (5-20 min). Such occurrences result in a confusing and messy increase and then decrease in the baseline. Such peaks can be hurried through the system by turning the GC column to 140°C until the peak emerges, and then reducing the temperature back to 110°C before resuming analysis.

13.0 CALCULATIONS AND DATA HANDLING

- 13.1 After review, enter final results into the LIMS system. Using the Copy, Paste Special (values only) feature, enter the sample concentrations from the spreadsheet into the Data Import file of LIMS. Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. There is less certainty in these data and, if sufficient sample and holding time are available, should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data are in the Analytical Data Entry – Wet Chemistry SOP.
- 13.2 LIMS calculates the final sample concentration as follows:
- 13.3 Calculate the following parameters for each analytical batch:
 - 13.3.1 Ethylation blank ($n = 1$) or the mean ethylation blank ($n > 1$)
 - 13.3.2 Ethylation-blank subtracted calibration factor for each standard (C_{fx} , Section 10.1.3) and peak measurement for each sample (R_s)

- 13.3.3 The mean calibration factor (CF_M), standard deviation of the calibration factor (SD), and relative standard deviation (RSD) of the calibration factor (Section 10.1.1.4).

$$\text{Calibration Factor} = \frac{R_s - R_e}{C_s}$$

R_s = Peak height or area of the standard

R_e = Peak height or area of the ethylation blank

C_s = Concentration of the standard (ng/L)

- 13.4 Compute the concentration of CH_3Hg in ng/L (parts-per-trillion; ppt) according to the following equation:

$$[CH_3Hg] \text{ (ng/L)} = \frac{R_s - R_e}{CF_M \times V}$$

Where:

R_s = gross peak height (or area) of signal for CH_3Hg in sample

R_e = peak height (or area) of signal for CH_3Hg in ethylation blank ($n = 1$) or mean ethylation blank ($n > 1$)

CF_M = mean calibration factor

V = Sample volume (L)

- 13.5 The CH_3Hg concentration of the mean ($n=3$ or more) method blank (ng/L, Equation 4) should be subtracted from the sample concentration calculated above to obtain the net in situ CH_3Hg concentration

$$[CH_3Hg]_{MB} \text{ (ng/L)} = \frac{R_{MB} - R_{EB}}{CF_M \times V_{MB}} \times \frac{V_{MB}}{V_s}$$

where:

R_{MB} = gross peak height (or area) of signal for CH_3Hg in the mean method blank

R_{EB} = gross peak height (or area) of signal for CH_3Hg in the ethylation blank ($n = 1$) or the mean ethylation blank ($n > 1$)

CF_M = Mean calibration factor

V_{MB} = Volume of the method blank

V_s = Volume of the sample

$$[CH_3Hg]_{net} = [CH_3Hg]_{sample} - [CH_3Hg]_{MB}$$

where:

$[CH_3Hg]_{net}$ = net in situ CH_3Hg concentration (ng/L)

$[CH_3Hg]_{sample}$ = ethylation-blank corrected concentration of CH_3Hg in the sample (ng/L)

$[CH_3Hg]_{MB}$ = concentration of CH_3Hg in the mean method blank (ng/L)

- 13.6 Reporting

- 13.6.1 All results are reported after subtraction of mean method blanks.
- 13.6.2 Under the conditions described here, the distillation procedure is not 100% efficient in recovering CH₃Hg because not all of the sample volume can be distilled, to avoid distillation of HCl. Laboratories should calculate the efficiency of the distillation for their laboratory. This calculation is done by keeping a running mean of the last 30 recoveries calculated for precision and recovery samples (IPR and OPR), excluding all values that are more than two standard deviations from the mean. Since the distillation technique is inherently and reproducibly non-quantitative, all results should be recovery corrected by an empirically derived factor.

$$F = \frac{100}{R}$$

Where:

F = Empirically derived correction factor

R = Recovery (the running mean of the last 30 IPR and OPR samples)

- 13.7 After review, enter final results into the LIMS system. Results flagged by the LIMS with an "E" qualifier are above the linear range of the instrument. There is less certainty in these data and, if sufficient sample and holding time are available, should be reanalyzed at an appropriate dilution. Details on the procedure for entering analytical data are in the Analytical Data Entry – Metals Section SOP. The peak integrations must be performed according to the Manual Integration of Chromatographic Peaks SOP.

14.0 METHOD PERFORMANCE

- 14.1 Initial Demonstration of Capability study data, Method Detection Limit study data and Performance Testing study data are maintained and available from the QA office.

15.0 POLLUTION PREVENTION

- 15.1 The quantity of chemicals purchased should be based on expected usage during their shelf life and the disposal cost of unused material.
- 15.2 Prepare the minimum amount of reagent and standard necessary.

16.0 WASTE MANAGEMENT

- 16.1 Refer to the Sample Disposal SOP for guidance on the disposal of any resulting residue, digestate, distillate, extract or standard.

17.0 REFERENCES

- 17.1 USEPA Method 1630, January 2001

17.2 USEPA Method 1669

17.3 Microbac Laboratories Quality Assurance Plan, current revision, all sections

18.0 TABLES, FORMS, CHECKLISTS, AND OTHER ATTACHMENTS

DRAFT

Method 1630

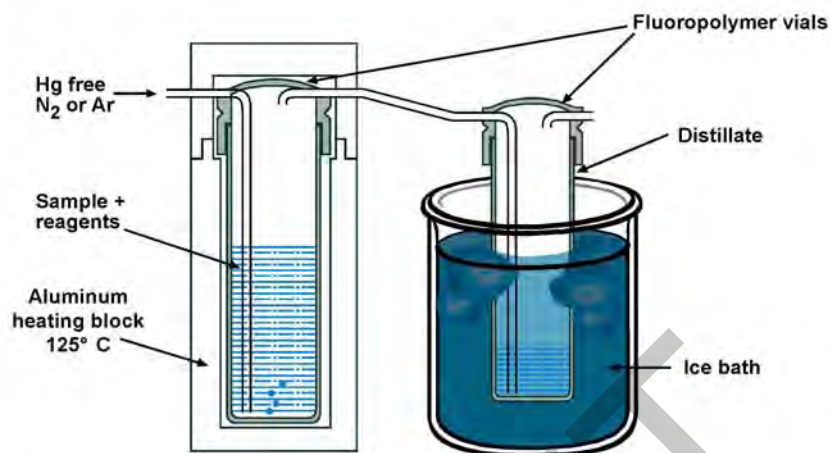


Figure 3 Schematic diagram showing the CH₃Hg distillation set-up.

Method 1630

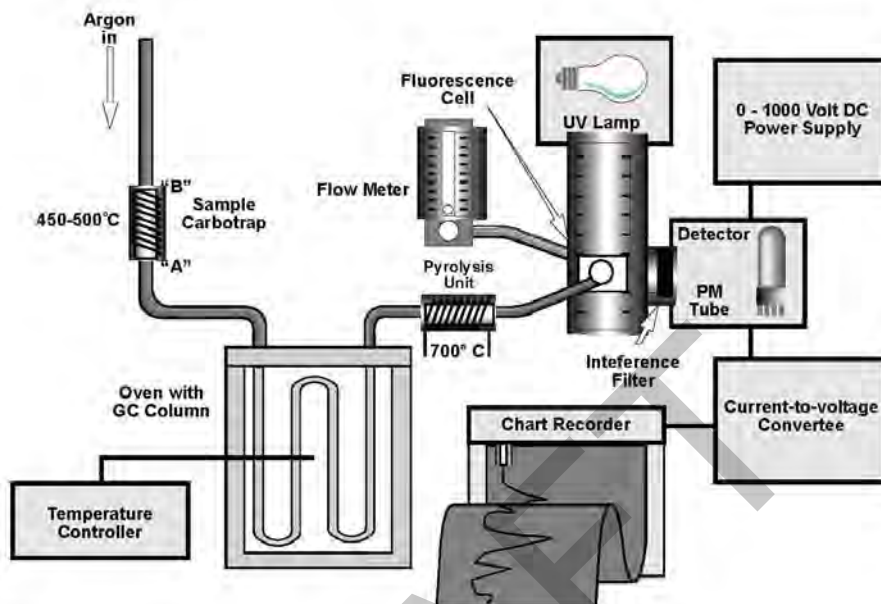


Figure 1 Schematic Diagram of the Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) Detector interfaced with the isothermal GC and pyrolytic decomposition column.

Draft, January 2001

Method 1630

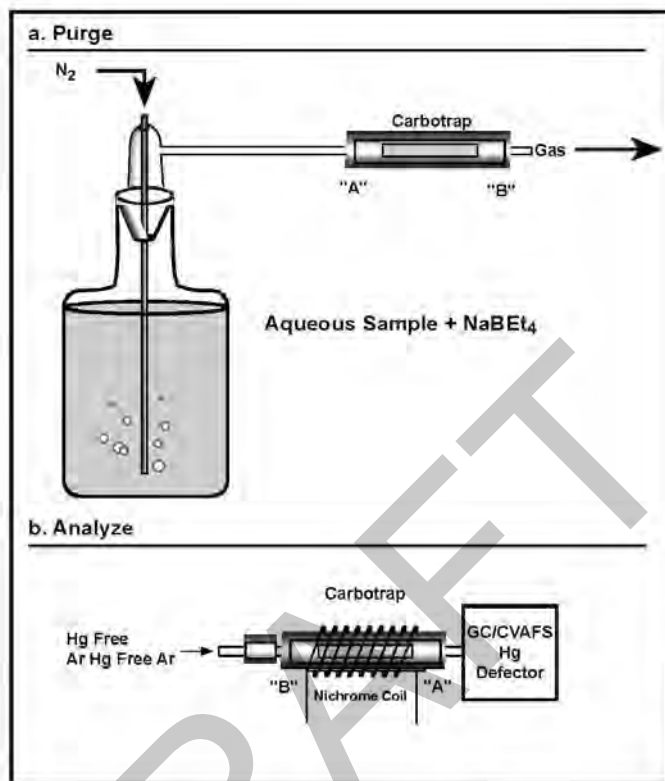


Figure 2 Schematic Diagram of Bubbler Setup (a), and Carbotrap® trap orientation (b).

Appendix N
Laboratory SOPs

DESA SOP
SOP C-96, Revision 2.1

Hexavalent Chromium



SOP #: C-96
Effective Date: 1/31/2009
Revision #: 2.1
Page 1 of 13

STANDARD OPERATING PROCEDURE
HEXAVALENT CHROMIUM

Signature and Title

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Review

Reviewed by:

Signature

Date

Reviewed by:

Signature

Date

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION 2
DIVISION OF ENVIRONMENTAL SCIENCE AND ASSESSMENT
LABORATORY BRANCH

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12. Data Analysis and Calculations
13. Method Performance
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STANDARD OPERATING PROCEDURE
HEXAVALENT CHROMIUM

1. SCOPE AND APPLICATION

- 1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes and is suitable for all concentration ranges up to 1000 µg/L. Higher concentrations can be analyzed by diluting the samples.
- 1.2 The reporting limit for this method is 10 µg/L.
- 1.3 This SOP is based on Hach Method 8023.
- 1.4 All analysts must satisfactorily perform a demonstration of capability (DOC) by meeting the method performance criteria in section 13.1 prior to performing sample analysis using this SOP.

2. SUMMARY OF METHOD

Hexavalent chromium is determined colorimetrically by reaction with diphenylcarbazide in acid solution.

3. DEFINITIONS

See SOP # G-15 for definitions.

4. INTERFERENCES

The reaction with diphenylcarbazide is nearly specific for chromium. Hexavalent molybdenum and mercury salts will react to form color with the reagent but the intensities are much lower than that for chromium at the specified pH.

5. SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be kept to an absolute minimum by following the appropriate standard safety procedures, e.g. wear proper protective equipment, gloves, lab coat, and working inside hoods whenever possible. Refer to Edison Facility Safety Manual Region II, Part 2 -

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Laboratory Safety for specific guidelines.

6. **APPARATUS AND MATERIALS**

- 6.1 Spectrophotometer, set at 540 nm
- 6.2 Miscellaneous laboratory apparatus such as volumetric pipettes, flasks, etc.

7. **REAGENTS AND SOLUTIONS**

7.1 Reagents

- 7.1.2 Chroma Ver 3 Pillows, 25 ml size, available from Hach Co.

7.2 Standard Preparation

- 7.2.1 Stock Hexavalent Chromium, 1000 mg/L
Purchased from a commercial source such as Hach Co.
- 7.2.2 Intermediate Standard, 10 mg/L
Dilute 1 ml of stock standard (7.2.1) into 100 ml of DI water.
- 7.2.3 Working Standards
Dilute the following ml of intermediate standard. (7.2.2) to 100 ml with distilled water. The upper and lower value of the standard curve should not be modified. If a project requires a different range the upper and lower standards may be modified but the reporting limit must also be adjusted accordingly. Samples above the high standard (+10%) must be diluted. The mid-range standards listed below are recommended but may be modified by the analyst.

<u>ml Working Stock</u>	<u>µg/L Hexavalent Chromium</u>
0.1	10
0.5	50
1.0	100
2.0	200
4.0	400
8.0	800
10.0	1000

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7.2.4 AQC Solution

Obtain solutions from ERA, EMSL or other reliable sources. Prepare according to instructions supplied by the supplier.

8. **SAMPLE COLLECTION, PRESERVATION, STORAGE & HOLDING TIME**

Samples may be collected in plastic or glass containers and must be analyzed within 24 hours of collection. If storage is required, samples should be stored in a refrigerator at 4°C.

9. **SAMPLE PREPARATION**

Samples may be filtered to remove turbidity.

10. **INSTRUMENT OPERATING CONDITIONS**

10.1 Hach DR/3000 Spectrophotometer

10.1.1 Turn on the spectrophotometer and the PC. Open both the HachLink software and Excel.

10.1.2 Press the zero button and then the absorbance button on the spectrophotometer. Enter your operator name in HachLink. Open the spreadsheet CR6 in Excel.

10.2 Hach DR/4000 Spectrophotometer

10.2.1 Turn on the spectrophotometer and the PC. Open the HachLink 2000 software. Open the CR6temp file in Excel. An empty window in tabled format should open.

10.2.2 From the main menu on the spectrophotometer, press the softkey under single wavelength. Press goto wavelength. Enter 540 and enter.

10.2.3 Press Exit and go to main menu.

12. **SAMPLE ANALYSIS**

11.1 Hach DR/3000 Spectrophotometer

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- 11.1.1 Pipette 25 mL of each calibration standard into a labeled square plastic spectrophotometer tube. Add the contents of 1 ChromVer 3 pillow, cap and invert several times. Press 5.00 and then start timer to set the timer for the 5 minute color development.
- 11.1.2 Place the next standard into the sample cell and cover. Enter the standard concentration under sample in the HachLink software and click on the capture button.
- 11.1.3 Repeat step 11.1.2 with the remaining standards. Highlight all of the columns in HachLink and click on edit and then copy. Go to the CR6 template in Excel and paste the information from HachLink.
- 11.1.4 Verify that the correlation coefficient is ≥ 0.995 .
- 11.1.5 Prepare the AQC's and samples as above in step 11.1.1. Return the HachLink and place the first AQC tube into the spectrophotometer. Enter the sample ID, cover and click on capture.
- 11.1.6 Repeat this process until all of the samples and associated QC are analyzed.

11.2 Hach DR/4000 Spectrophotometer

- 11.2.1 Pipette 25 mL of each calibration standard into a labeled square plastic spectrophotometer tube. Add the contents of 1 ChromVer 3 pillow, cap and invert several times. Press 5.00 and then start timer to set the timer for the 5 minute color development.
- 11.2.2 After the timer sounds, place the 0 standard into the spectrophotometer. Press the options key and press sample. Enter a sample ID between 1-9999. Use 1 for the 0 standard and correct later in Excel. Press enter.
- 11.2.3 Press the print key and full table to send the readings to Hachlink. If sample information does not appear on the computer screen, check the connections and software settings.
- 11.2.4 Place the next standard into the sample cell and cover.
- 11.2.5 Repeat step 11.2.1-11.2.3 with the remaining standards. Double click on the Hachlink standards data. The software will automatically open a second Excel spreadsheet (Book 1) and enter the standards information

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from Hachlink.

- 11.2.6 Highlight, copy and paste the header and standards data into the CR6 template.
- 11.2.7 Correct the true value of the 0 standard from 1 to 0 and verify that the correlation coefficient is >0.995 .
- 11.2.8 Prepare and analyze the AQC's and samples as above repeating the process until all of the samples and associated QC are analyzed. If any of the samples are colored or turbid, aliquot another 25 mL of sample into a separate labeled square plastic spectrophotometer tube. Analyze these aliquots without the addition of a ChromVer 3 pillow .
- 11.2.9 After the analysis is complete, go to the Hachlink generated Excel spreadsheet. Highlight, copy and paste all of the rows with the sample information from the data column on the left to the units column.
- 11.2.10 Return to the CR6 template and paste the information in the sample section of the spreadsheet.
- 11.2.11 Enter any sample dilutions manually and enter the full sample ID's in place of the 4 digit numbers from the spectrophotometer into the CR6 template. Rename the spreadsheet in the format of MM/DD/YYSO4.

13. DATA ANALYSIS AND CALCULATIONS

All calculations are performed in the Excel spreadsheet. A linear regression is used to calculate sample results in mg/L by using the absorbances of samples and standards. Multiplication for sample dilutions and the subtraction of the color/turbidity blank results must be done manually in Excel.

14. METHOD PERFORMANCE

A demonstration of capability (DOC) should be performed each time there is a significant change in the chemistry of the method, a major modification to an existing instrument, or a new instrument is installed. A DOC is performed by each analyst designated to analyze samples using this method. An annual check must subsequently be performed and documented for each analyst using this method.

13.1 Accuracy and Precision

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13.1.1 Demonstration of Capability

A demonstration of capability study must be performed and documented for each analyst using this method. The study should consist of the analysis of four standards which are from a source independent of the standard curve. The results of the standards must be within the acceptance criteria supplied by the manufacturer or within 20% if none are specified. The % RSD should be within 20%. The results of the accuracy and precision study (true value, % recovery, standard deviation and % RSD) are maintained by the Quality Assurance Officer for each analyst and are located in the Central Branch File.

13.1.2 Continuing Demonstration of Capability

An annual continuing demonstration of capability study must be performed and documented. It may consist of either successfully analyzing a PT sample or analyzing 2 sets of AQC standards to within control limits as stated in section 13.1.1. The results of the continuing accuracy and precision study (true value, % recovery, standard deviation and % RSD or final report from the PT provider) are maintained by the Quality Assurance Officer for each analyst and are located in the Central Branch File.

13.2 Method Detection Limit (MDL)

An MDL Study was conducted for this method. The study is based on the requirements listed in 40 CFR Part 136 Appendix B. Specific procedures for conducting an MDL study can be found in SOP # G-8. The MDL Study comprised the analysis of seven reagent grade water samples fortified at a level between 2-3x the detection limit. The results of the MDL determination (true value, average concentration, standard deviation and calculated MDL) are maintained by the Quality Assurance Officer for each method and are located in the Central Branch File.

13.3 Limit of Quantitation (LOQ)

The Laboratory performs a Limit of Quantitation (LOQ) study on an annual basis for analytes associated with chemistry methods. The validity of LOQ is confirmed by successful analysis of a Laboratory Fortified Blank (LFB) at approximately 2X the reporting limit. The acceptance criteria for each analyte is $\pm 30\%$ of the true value. After this study is completed, it is reviewed and approved by the Laboratory Management. A summary of all LOQ study performance is maintained in the Laboratory's Central File.

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14. QUALITY CONTROL

14.1 Calibration Curve

Acceptance Criteria - A minimum of 5 standards and a blank must be used to generate the calibration curve. The correlation coefficient must be ≥ 0.995 .

Corrective Action - If the correlation coefficient of the calibration curve, consisting of at least five standards and a blank, is < 0.995 , the calibration is disallowed. The analysis must be terminated, and repeated after correcting the problem.

14.2 Instrument Performance Check (IPC) Standard or Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV) Standard.

Acceptance Criteria - Analyze the IPC solution for all determinations immediately following each calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution immediately following calibration must verify that the instrument is within $\pm 10\%$ of the true value. Subsequent analyses of the continuing IPC solution must be within $\pm 10\%$ of the true value.

Corrective Action - If the calibration cannot be verified within the specified limits, analysis must be discontinued, the cause determined and/or in the case of drift the instrument re-calibrated. All samples following the last acceptable IPC solution must be reanalyzed.

14.3 Laboratory Reagent Blank (LRB), Prep Blank (PB), Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

Acceptance Criteria - Analyze a blank along with each batch of 20 or fewer samples. All LRB/PB/ICB/CCB results must be $<$ the Reporting Limit.

Corrective Action - If the results of the LRB/PB/ICB/CCB are $>$ the Reporting Limit then all associated samples with a concentration of $\leq 10\times$ the amount found in the LRB/PB/ICB/CCB should be reprepared and reanalyzed (sample results $\geq 10\times$ the amount found in the LRB/PB/ICB/CCB are not considered to be affected by the blank contamination or drift).

If the samples cannot be reprepared, then all affected sample results must be either 1) qualified accordingly, or 2) the reporting limit is raised to the amount found in the blank. Check with the team leader/section chief to determine which option

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should be used.

14.4 Laboratory Fortified Blank (LFB), Analytical Quality Control Samples (AQC's) or Quality Control Samples (QCS)

Acceptance Criteria - Analyze two LFB/AQC/QCS samples with each batch of 20 or fewer samples. Calculate accuracy as percent recovery using the following equation:

$$\% \text{ Recovery} = \frac{\text{LFB/AQC/QCS}}{s} \times 100$$

where:

LFB/AQC/QCS = control sample results determined by laboratory

s = concentration equivalent of analyte added to fortify the LFB/AQC/QCS solution.

The % recovery of the LFB/AQC/QCS should be within the control limits specified by the manufacturer. The relative percent difference (RPD) of the duplicates should not exceed 20% for aqueous standards.

Corrective Action - If the % recovery or RPD results are outside the required control limits, the affected samples should be reprepared and reanalyzed. If the samples cannot be reprepared, then all affected sample results must be qualified accordingly.

14.5 Laboratory Fortified Matrix(LFM) or Matrix Spike(MS) Recovery

Acceptance Criteria - Add a known amount of the target analyte to a minimum of one sample per batch of 20 or less samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. Calculate the percent recovery, corrected for background concentration measured in the unfortified sample aliquot as per the equation below. The % recovery should be 80-120%.

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$$R = \frac{C_s - C}{s} \times 100$$

where: R = percent recovery,
Cs = fortified sample concentration,
C = sample background concentration, and
s = conc. equivalent of spike added to sample.

Corrective Action - If the % recovery of the LFM/MS is outside the required control limits, and the laboratory performance is shown to be in control, the recovery problem encountered is judged to be matrix related, not system related. The native sample result of the sample used to produce the LFM/MS must be qualified accordingly.

Note: The % recovery of the LFM/MS is not evaluated if the result of the unfortified sample concentration is $\geq 1X$ the level used to fortify the sample.

15. REPORTING AND VALIDATION

15.1 Reporting Limits

The reporting limits are calculated based on the concentration of the lowest calibration standard analyzed. The reporting limits are matrix and dilution dependent. All results are reported to 2 significant figures.

15.2 Sample Data Package

The sample data package should include the following items, where applicable. The analyst may also include other information that may be pertinent to the analysis such as project narratives, etc.

1. Sample preparation information
2. Sample analysis data
3. Instrument calibration data
4. Instrument/computer printouts
5. Data summary checklist with all relevant information entered

15.3 Laboratory Information Management System (LIMS)

The analyst enters the data on the LIMS under the appropriate analytical codes.

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15.4 Data Validation

The data package is given to the reviewer. The review is done by a peer who was not involved in the analysis. Upon completion of the review, including validation of all the appropriate codes in the LIMS for the particular project(s), the data reviewer will sign and date the QA/QC Checklist.

15.5 Data Records

A copy of each analytical data package is made for each project in the package and placed in the bin identified for the designated project file. The records for this designated project file are filed in our locked record cabinets once all data from the project, e.g., non-metal inorganic data, organic data, microbiology data, etc. has been reviewed by the appropriate staff.

16. POLLUTION PREVENTION

- 16.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the USEPA recommends recycling as the next best option.
- 16.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.
- 16.3 For information about pollution prevention consult the EPA Edison Facility Pollution Prevention Plan in Compliance with Executive Order 12856.

17. WASTE MANAGEMENT

The USEPA requires that laboratory waste management practice be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any water discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal

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restrictions. For further information on waste management consult the Region 2 SOP G-6, "Disposal of samples and hazardous wastes in Regional Laboratory".

18. **REFERENCES**

- 18.1 Hach DR/4000 Spectrophotometer Instrument Manual, 2nd ed., Revision 2, 11/99, Method 8023
- 18.2 Standard Methods for the Examination of Water and Wastewater, Method 3500-Cr B., 20th Edition, 1998

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REQUEST FOR SOP CHANGE

Initiator Name: Deborah Kay

Date of Initiation: 4/8/2010

Dept: San

SOP Title: See attached list

SOP #: See attached list Revision #: See attached list

Please Check One

MINOR REVISION ☒

MAJOR REVISION ☐

CHANGE(S) (Use attachment if necessary):

Change AQC control limits for most sanitary analyses for Non-NPDES and Non-Drinking Water from vendor supplied limits to in-house set limits.

REASON(S) FOR CHANGE(S):


APPROVAL:

NAME:

Signature/Date

EPA Section Chief/Team Leader

Jim Ferrett

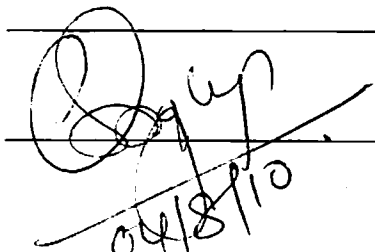
 4/8/10

ESAT Analytical Supervisor/QAO

EPA Task Order Project Officer

Effective Date: May 1, 2010

Sumy Cherukara
EPA QAO

 04/8/10

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USEPA Region 2 Laboratory
Revised 07/31/08

Proposed AQC limits for Non-NPDES, Non-Drinking Water analyses

PARAMETER	SOP ID	METHOD	Current limits	New Limits
ALKALINITY	C-18	SM 2320 B	ERA	85-115%
AMMONIA	C-80	EPA 350.1	ERA	85-115%
BOD	C-21	SM 5210 B	84.6-115.4	No Change
Bromide (IC)	C-94	EPA 300.0	ERA	85-115%
CHLORIDE	C-22	SM 4500 Cl C	ERA	85-115%
CL(IC)	C-94	EPA 300.0	ERA	85-115%
COD	C-53	EPA 410.4	ERA	85-115%
CR+6	C-96	SM 3500 Cr D	ERA	85-115%
CYANIDE	C-28	EPA 335.4	ERA	85-115%
FLUORIDE(IC)	C-94	EPA 300.0	ERA	85-115%
FLUORIDE(LT)	C-93	USGS-I-4327-85	ERA	85-115%
IGNITABILITY	C-23	ASTM D93-08	ERA	85-115%
MBAS	C-61	SM 5540 C	ERA	85-115%
NITROGEN	C-79	31-107-04-4-A	ERA	85-115%
NO2	C-79	EPA 353.2	ERA	85-115%
NO2(IC)	C-94	EPA 300.0	ERA	85-115%
NO3	C-79	EPA 353.2	ERA	85-115%
NO3(IC)	C094	EPA 300.0	ERA	85-115%
NO3+NO2	C-79	EPA 353.2	ERA	85-115%
O-PO4	C-68	EPA 365.1	ERA	85-115%
O-PO4 (IC)	C-94	EPA 300.0	ERA	85-115%
	C-			No Change
OIL & GREASE	126	EPA 1664A Automated	78-114%	
pH/Corrosivity	C-24	SM 4500 H+B	ERA	98-102%
PHENOL	C-29	EPA 420.4	ERA	85-115%
SO4(IC)	C-94	EPA 300.0	ERA	85-115%
	C-			
SULFIDE(MB)	115	SM 4500-S2D	ERA	85-115%
Sulfate (Spec)	C-19	ASTM D516-02	ERA	85-115%
	C-			No Change
TPH	126	EPA 1664A Automated	64-132%	
T.PHOS	C-68	EPA 365.1	ERA	85-115%
TKN	C-40	EPA 351.2	ERA	85-115%
TOC	C-83	SM 5310 B	ERA	85-115%
TDS	C-37	SM 2540 C	ERA	85-115%
TSS	C-33	SM 2540 D	ERA	85-115%

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Laboratory Branch

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%WATER	C-118	Hydroscout	80-120	85-115%
CYANIDE (sediment)	C-28	EPA 335.4	ERA	75-125%
TOC (sediment)	C-88	SM 5310 B	ERA	75-125%

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REQUEST FOR SOP CHANGE

Initiator Name: Deborah Kay

Date of Initiation: 12/31/09

Dept: Sanitary

SOP Title: Hexavalent Chromium

SOP #: C-96 Revision #: 2.1

Please Check One

MINOR REVISION ☒

MAJOR REVISION ☐

CHANGE(S) (Use attachment if necessary):

Add to Section 11 the following or similar statement:

Any reportable result for Hexavalent Chromium greater than the reporting limit must be confirmed via ICP-AES or ICP-MS before validation in the LIMs.

Add to Section 7.2.4 a section stating that the AQC must be prepared from a source separate from the calibration standards.

Edit Section 14.3 similarly to the following:
Analyze a blank after each CCV.

Please note the blank section can be applied to Sanitary methods such as Cyanide, NO3/NO2, TKN, COD, etc. – methods requiring calibration.

REASON(S) FOR CHANGE(S): Confirmation of Cr6+ and ICV clarification.

APPROVAL:

NAME:

Signature/Date

EPA Section Chief/Team Leader

James Ferrell

[Signature] 1/14/10

ESAT Analytical Supervisor/QAO

EPA Task Order Project Officer

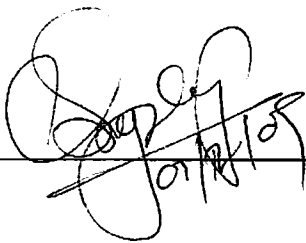
Smy Chesukang

[Signature] 1/14/10

USEPA Region 2 Laboratory
Revised 07/31/08

Effective Date: 01/12/09

Sumy Cherukara
EPA QAO


01/12/09

Appendix N
Laboratory SOPs

DESA SOP
C-33 Modified, Revision 3.1

Suspended Solids Concentration (SSC or TSS)
By SM 2540-D



SOP #: C-33
Effective Date: 1/31/2009
Revision #: 3.1
Page 1 of 12

STANDARD OPERATING PROCEDURE

TOTAL SUSPENDED SOLIDS (TSS) VOLATILE SUSPENDED SOLIDS (VSS)

Signature and Title

Prepared by: Deborah Kay
Deborah Kay, Env. Scientist, SCMS

1/22/09
Date

Peer Reviewed by: Jamie Hale
Jamie Hale, Chemist, SCMS

1/23/09
Date

QA Reviewed by: Somy Cherukara
Somy Cherukara, Quality Assurance Officer

1/30/09
Date

Approved by: James Ferretti
James Ferretti, Team Leader, SCMS

1/30/09
Date

Approved by: John Bourbon
John Bourbon, Acting Chief, Laboratory Branch

1/30/09
Date

Review

Reviewed by: _____
Signature

Date

Reviewed by: _____
Signature

Date

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION 2
DIVISION OF ENVIRONMENTAL SCIENCE AND ASSESSMENT
LABORATORY BRANCH

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12. Data Analysis and Calculations
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17. Waste Management
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STANDARD OPERATING PROCEDURE
TOTAL SUSPENDED SOLIDS (TSS)
VOLATILE SUSPENDED SOLIDS (VSS)

1. SCOPE AND APPLICATION

- 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
- 1.2 The reporting limit for this method is 10 mg/L when a 100 ml sample volume is used. At client request, a 1.0 mg/L reporting limit is sometimes reported when 1 L of sample is used for analysis.
- 1.3 This SOP is based on Standard Methods 2540 D and 2540 E.
- 1.4 All analysts must satisfactorily perform a demonstration of capability (DOC) by meeting the method performance criteria in section 13.1 prior to performing sample analysis using this SOP.

2. SUMMARY OF METHOD

- 2.1 A well-mixed sample is filtered through a glass fiber filter. The residue retained on the filter is dried to a constant weight at 103-105°C. If VSS is required, the filter is also weighed after being placed in a muffle furnace.
- 2.2 The filtrate from this method may be used for Total Dissolved Solids analysis. (SOP C-37)

3. DEFINITIONS

See SOP # G-15 for definitions.

4. INTERFERENCES

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- 4.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.
- 4.2 Samples high in filterable residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing the filter of any dissolved solids (Section 7.1) minimizes this potential interference.

5. SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be kept to an absolute minimum by following the appropriate standard safety procedures, e.g. wear proper protective equipment, gloves, lab coat, and working inside hoods whenever possible. Refer to Edison Facility Safety Manual Region II, Part 2 - Laboratory Safety for specific guidelines.

6. APPARATUS AND MATERIALS

- 6.1 Glass fiber filter discs without organic binder, such as Millipore AP-40, Reeve Angel 934-AH, Gelman type A/E, or equivalent
- 6.2 Filter Support: filtering apparatus with reservoir and a coarse (40-60 microns) fritted disc as a filter support
- 6.3 Suction flask
- 6.4 Drying oven, 103-105°C
- 6.5 Desiccator
- 6.6 Analytical balance, capable of weighing to 0.1 mg
- 6.7 Muffle furnace, 550 °C.

7. REAGENTS AND SOLUTIONS

- 7.1 Deionized water
- 7.2 AQC Solution

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Obtain solutions from ERA or other reliable sources.

8. SAMPLE COLLECTION, PRESERVATION, STORAGE & HOLDING TIME

- 8.1 Non-representative particulate matter such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
- 8.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended. Samples must be analyzed within 7 days of collection

9. SAMPLE PREPARATION

Samples must be vigorously shaken prior to analysis.

10. INSTRUMENT OPERATING CONDITIONS

Not applicable

11. SAMPLE ANALYSIS

- 11.1 Prepare the glass fiber filter discs by placing the glass fiber filter on the filtering apparatus with wrinkled surface up. While vacuum is applied, wash the filter with three successive 20 mL volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus place into a numbered aluminum dish. Dry in an oven at 103-105°C for one hour. If samples require analysis for VSS, place rinsed filters in a muffle furnace at 550° C for a minimum of 1 hour. When labeling weighing dishes used for VSS, use a heat resistant marker or use a ball point pen to indent the identifying labels into the dish tabs. Remove to desiccator and store until needed.
- 11.2 All filter weights are entered into an Excel spreadsheet which will calculate the TSS values automatically. To access and set up the spreadsheet and balance, turn on the PC in the balance room.

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- 11.3 Click on the Mettler icon. Once the Mettler screen appears, click on the down arrow to close the window. After this is done, confirm that the balance shows the symbol I/O on its display indicating that the computer and balance are linked.
- 11.4 Click on the Excel icon and pull up the spreadsheet named TSS.
- 11.5 Enter the sample/project information at the top of the screen and enter the sample ID's where indicated. Tare the balance and place the cursor on Filter Tare Weight. Place the filter on the balance and once a stable reading is obtained, hit the print key on the balance. This will automatically enter the reading from the balance onto the spreadsheet. After all of the filters have been weighed, save the spreadsheet in Excel using the following guidelines, MM/DD/YYTSS.
- 11.6 Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Print out the preliminary spreadsheet and return to the laboratory.
- 11.7 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.
- 11.8 Shake the sample vigorously and transfer the sample to the filter using a graduated cylinder. Filter 100 mL of sample through each filter paper. Remove all traces of water by continuing to apply vacuum after sample has passed through. If a 1.0 mg/L reporting limit has been requested, 1L of sample should be filtered.

NOTE: When filtering samples that look like they may have high TSS values, do not add the entire 100 mL sample volume to the filtering apparatus at once. Instead, fill up the 100 mL graduate cylinder and slowly pour the sample into the funnel. Do not pour so slowly that the sample has time to settle in the cylinder. When the filtration begins to slow, stop pouring and record the sample volume used.

- 11.9 With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through. Record the sample volumes filtered on the spreadsheet.

NOTE: Total volume of wash water used should equal approximately 2 mL per cm². For a 4.7 cm filter the total volume is 30 mL.

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- 11.10 Remove filter from filtering apparatus and place into its aluminum dish. Dry at least one hour at 103-105°C. Cool in a desiccator.
- 11.11 Return to the Excel spreadsheet and weigh each filter paper. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).
- 11.12 If samples are also being analyzed for VSS, place filters in the muffle furnace for a minimum of 1 hour, cool. Return to the Excel spreadsheet and weigh each filter paper. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). The drying at 103-105°C can be eliminated if the filters will be muffled.
- 11.13 Verify that all QC samples are within the limits specified in section 14.

12. DATA ANALYSIS AND CALCULATIONS

The calculations used in the Excel spreadsheet are as follows:

$$\text{Non-filterable residue (TSS), mg/L} = \frac{(A - B) \times 1,000,000}{C}$$

where:

A = weight of filter + residue in g

B = weight of filter in g

C = mL of sample filtered

$$\text{Volatile suspended solids (VSS), mg/L} = \frac{(A - B) \times 1,000,000}{C}$$

where:

A = weight of filter + residue before ignition in g

B = weight of filter + residue after ignition in g

C = mL of sample filtered

13. METHOD PERFORMANCE

A demonstration of capability (DOC) should be performed each time there is a significant change in the chemistry of the method, a major modification to an existing instrument, or a new instrument is installed. A DOC is performed by each analyst designated to analyze

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samples using this method. An annual check must subsequently be performed and documented for each analyst using this method.

13.1 Accuracy and Precision

13.1.1 Demonstration of Capability

A demonstration of capability study must be performed and documented for each analyst using this method. The study should consist of the analysis of four standards which are from a source independent of the standard curve. The results of the standards must be within the acceptance criteria supplied by the manufacturer or within 20% if none are specified. The % RSD should be within 20%. The results of the accuracy and precision study (true value, % recovery, standard deviation and % RSD) are maintained by the Quality Assurance Officer for each analyst and are located in the Central Branch File.

13.1.2 Continuing Demonstration of Capability

An annual continuing demonstration of capability study must be performed and documented. It may consist of either successfully analyzing a PT sample or analyzing 2 sets of AQC standards to within control limits as stated in section 13.1.1. The results of the continuing accuracy and precision study (true value, % recovery, standard deviation and % RSD or final report from the PT provider) are maintained by the Quality Assurance Officer for each analyst and are located in the Central Branch File.

14. QUALITY CONTROL

14.1 Laboratory Reagent Blank (LRB) or Prep Blank (PB), IPB or Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

Acceptance Criteria - Analyze a blank along with each batch of 20 or fewer samples. All LRB/ICB/CCB/PB results must be < the Reporting Limit.

Corrective Action - If the results of the ICB/CCB/PB are > Reporting Limit then all associated samples with a concentration of $\leq 10x$ the amount found in the ICB/CCB/PB should be reprepared and reanalyzed (sample results $\geq 10x$ the amount found in the ICB/CCB/PB are not considered to be affected by the blank contamination or drift).

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If the samples cannot be reprepared, then all affected sample results must be either 1) qualified accordingly, or 2) the reporting limit is raised to the amount found in the sample. Check with the team leader/section chief to determine which option should be used.

14.2 Laboratory Fortified Blank (LFB) or Analytical Quality Control Samples (AQC's)

Acceptance Criteria - Analyze two LFB/AQC/QCS samples with each batch of 20 or fewer samples. Calculate accuracy as percent recovery using the following

$$\% \text{ Recovery} = \frac{\text{LFB/AQC/QCS}}{s} \times 100$$

equation:

where: LFB/AQC/QCS = control sample results determined by laboratory

s = concentration equivalent of analyte added to fortify the LFB/AQC/QCS solution.

The % recovery of the LFB/AQC/QCS must be within the acceptance criteria provided from the manufacturer. The relative percent difference (RPD) of the duplicates should not exceed 20% for aqueous standards.

Corrective Action - If the % recovery or %RPD results are outside the required control limits, the affected samples should be reprepared and reanalyzed. If the samples cannot be reprepared, then all affected sample results must be qualified accordingly.

14.3 Sample Matrix duplicates

Acceptance criteria - If enough sample is provided to the lab, analyze one sample in duplicate for each batch of 20 or less samples. The relative percent difference (RPD) of the duplicates should not exceed 20%.

Corrective action - If the %RPD results are greater than 20%, the affected samples should be reprepared and reanalyzed. If the samples cannot be reprepared, then all affected sample results must be qualified accordingly.

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15. REPORTING AND VALIDATION

15.1 Reporting Limits

The reporting limit for TSS is 10 mg/L using a 100 mL sample volume. Certain projects are reported using a 1.0 mg/L reporting limit and using a 1L sample volume. The reporting limits are matrix and dilution dependent. All results are reported to 2 significant figures.

15.2 Sample Data Package

The sample data package should include the following items, where applicable. The analyst may also include other information that may be pertinent to the analysis such as project narratives, etc.

1. Sample preparation information
2. Sample analysis data
3. Instrument calibration data
4. Instrument/computer printouts
5. Data summary checklist with all relevant information entered

15.3 Laboratory Information Management System (LIMS)

The analyst enters the data on the LIMS under the appropriate analytical codes.

15.4 Data Validation

The data package is given to the reviewer. The review is done by a peer who was not involved in the analysis. Upon completion of the review, including validation of all the appropriate codes in the LIMS for the particular project(s), the data reviewer will sign and date the QA/QC Checklist.

15.5 Data Records

A copy of each analytical data package is made for each project in the package and placed in the bin identified for the designated project file. The records for this designated project file are filed in our locked record cabinets once all data from the project, e.g., non-metal inorganic data, organic data, microbiology data, etc. has been reviewed by the appropriate staff.

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16. POLLUTION PREVENTION

- 16.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the USEPA recommends recycling as the next best option.
- 16.2 The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.
- 16.3 For information about pollution prevention that may be applicable to laboratories, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Regulations and Science Policy, 115 16th Street N.W., Washington D.C 20036, (202)872-4477.

17. WASTE MANAGEMENT

The USEPA requires that laboratory waste management practice be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The agency urges laboratories to protect the air, water and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any water discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the Region 2 SOP G-6, "Disposal of samples and hazardous wastes in Regional Laboratory".

18. REFERENCES

- 18.1 Standard Methods for the Examination of Water and Wastewater, Method 2540 D., Total Suspended Solids, 20th Edition, 1998

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SOP #: C-33
Effective Date: 1/31/2009
Revision #: 3.1
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- 18.2 Standard Methods for the Examination of Water and Wastewater, Method 2540 E.,
Fixed and Volatile Solids Ignited at 550 ° C., 20th Edition, 1998

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Appendix N

Laboratory SOPs

DESA SOP

Updated SOPs will be included in the Final QAPP for

Total Dissolved Solids (TSS)

Total Organic Carbons (TOC)

Dissolved Organic Carbons (DOC)

Particulate Organic Carbons (POC)